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NATO-CCMS Pilot Study on Disposal of Hazardous Wastes: Metal Finishing Wastes

Project Leader: France

NATO Committee on the Challenges of Modern Society, Brussels (Belgium)

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Aim of study was to investigate problems set up by metal finishing industries. It has proved worthwhile to overlap the treatment approach to hazardous waste; combining all activities, with the analytic approach of the industrial sectors which produce them.

KEYWORDS: *Hazardous materials, *Metal finishing, *Foreign technology.

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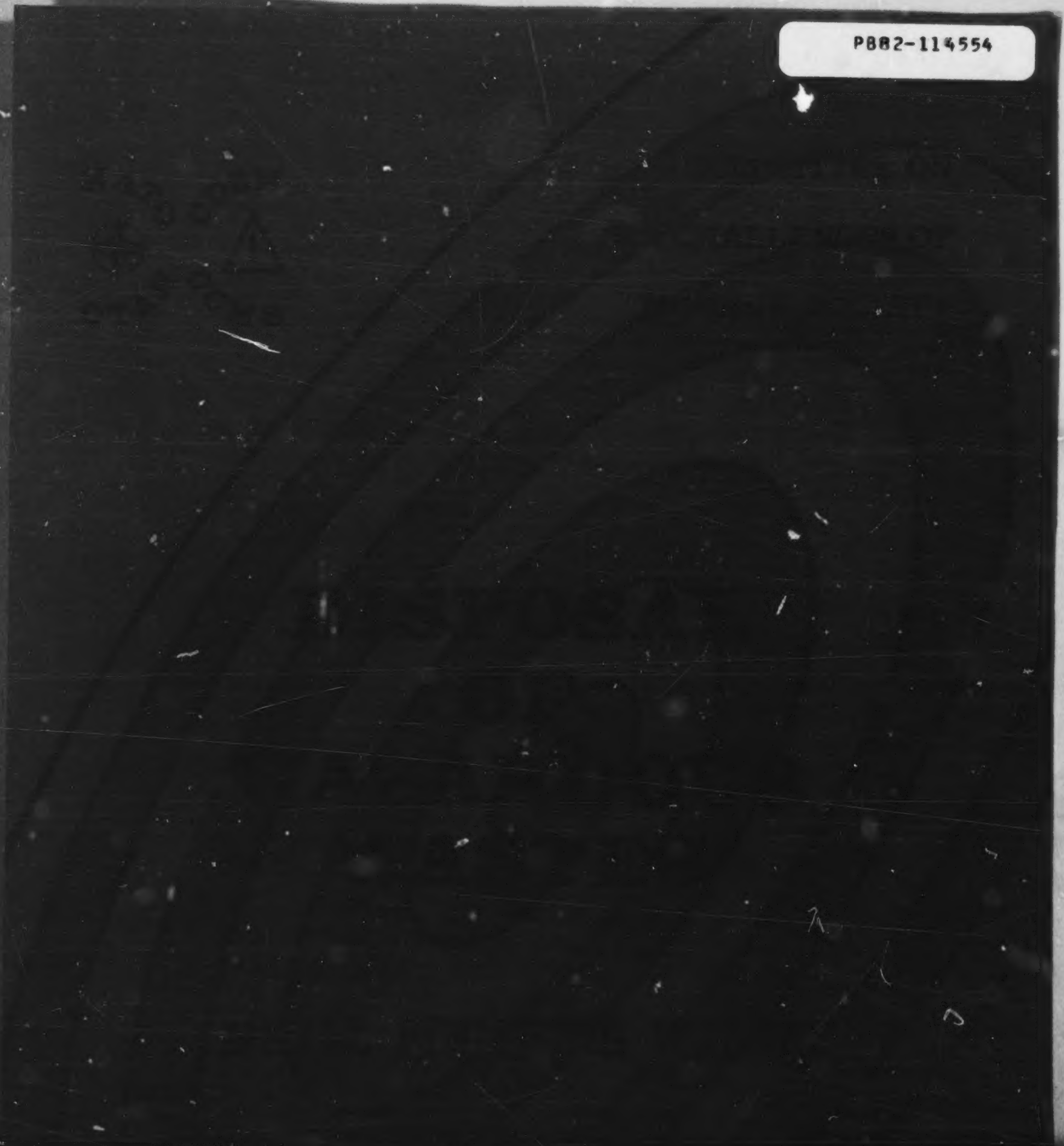

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METAL FINISHING WASTES

[illegible]

[illegible] ATLANTIC [illegible] ORGANIZATION

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COMMITTEE ON THE CHALLENGES OF MODERN SOCIETY
NORTH ATLANTIC TREATY ORGANIZATION

PILOT STUDY ON THE DISPOSAL OF HAZARDOUS WASTES

METAL FINISHING WASTES

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Final report prepared by FRANCE

- March 1981 -

☐ 100 % RECYCLED PAPER

Umweltschonend hergestelltes Papier

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PREFACE

Within the framework of the Committee on the Challenges of Modern Society of NATO, and following its report concerning the chromium cycle, France put forward the "Pilot Study on the Disposal of Hazardous Wastes", to make a contribution to its work by investigating problems set up by metal finishing industries. It has, in fact, proved worthwhile to overlap the treatment approach to hazardous waste, combining all activities, with the analytic approach of the industrial sectors which produce them.

Two studies were commissioned by the "Ministère de l'Environnement et du Cadre de Vie" :

- an aggregate analysis of problems connected to waste production by metal finishing activities, carried out by "Société CEPLAM"

- a study assigned to "Société FAIRTEC", which is more especially concerned with methods of preventing hazardous waste production.

The scope of this report concluding the scheme on metal finishing waste has been much extended thanks to important contributions from the U.S.A., United Kingdom, Netherlands, Canada and Federal Republic of Germany.

This exchange of informations has emphasized the constant factors of this branch of activities and allowed for a better understanding of the impact of technological progress and cost evolution in that area.

The contributions from the various countries to this report are mainly the following (the bibliography contains references for the main quoted works, except for the documents which were specially prepared for the project on metal finishing wastes) :

- From the Federal Republic of Germany :
  - A first answer to the questionnaire sent in 1976 followed by an up to date answer in July of 1978 ;
  - An answer to the questionnaire sent in 1979 ;
  - A contribution "Waste free electroplating" and an information about the "DEGUSSA Process" (hardening process without cyanides) ;
  - A contribution about environmental legislation with regard to metal finishing waste.
- From the Netheelands :
  - An answer to the questionnaire sent in 1976 ;
  - An answer to the questionnaire sent in 1979 ;
  - A short communication about waste pickling acid from hot dip galvanizing.

- From the United Kingdom :

- An answer to the questionnaire sent in 1976 ;
- Waste Management Paper N° II : Metal Finishing Waste ;
- A lot of documents about control or purification of wastes.

- From Canada :

- Five reports from the Environmental Protection Service about regulations, codes and protocols applicable to recovery or disposal of metal finishing waste.

- From The U. S. A. :

- An answer to the questionnaire sent in 1976 ;
- "Development document for proposed existing source pre-treatment standards for the electroplating point source category" from the E.P.A. ;
Moreover, the E.P.A. supplied France with the translation of the interim report presented in Vancouver on the 5-9th of June 1979.

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- the bath characteristics
- location of the bath in the sequence
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SUMMARY

Any desire to modify one or several physical,chemical or electrical characteristics of a surface involves a process which will be, in fact, a treatment of this surface.

These operations are required for numerous industrial productions : automobile, aeronautics,engineering... Captive shops, which are part of a wider production process have to be distinguished from job shops the chief activity of which is metal finishing ; the latter are not so numerous as the former, and easier to identify. The large number of shops with a very low labour force or even without a wage earner is an essential datum of that activity.

Chemical or electrochemical processes usually employed for metal finishing, lead to considerable losses in costly or toxic substances. These substances are generally dissolved in water so diluted effluents (contents in mg/l) or concentrate ones (contents in g/l) may be obtained.

CONTROL OF LOSSES

Dilute effluents are mainly composed of spent waters from rinsing. Losses in additives may be considerably reduced in rinse waters by application of control techniques. These techniques are particularly recommended in case of sequences of plating operations for the deposit of a metal upon a substrate surface. The control of a substance loss means that an appropriate technique operates to prevent the substance from being unserviceable in its original state, in the sequence. The purpose of using these techniques is to decrease in pollution flow an to save raw materials.

The advantages of control :

- Saving raw materials,
- Decrease in water consumption,
- Improvment in maintenance technique of plating baths in most cases,
- Decrease in the size of effluent treatment facilities,
- Decrease in the consumption of reagents for effluent treatment,
- Decrease in the metal salt content after effluent treatment
- Decrease in sludge quantity requiring a disposal.

are such that they can result:

- in reducing costs of effluent and sludge treatment,
- in paying back to some extent the capital investment required for a satisfactory control.

RECOVERY

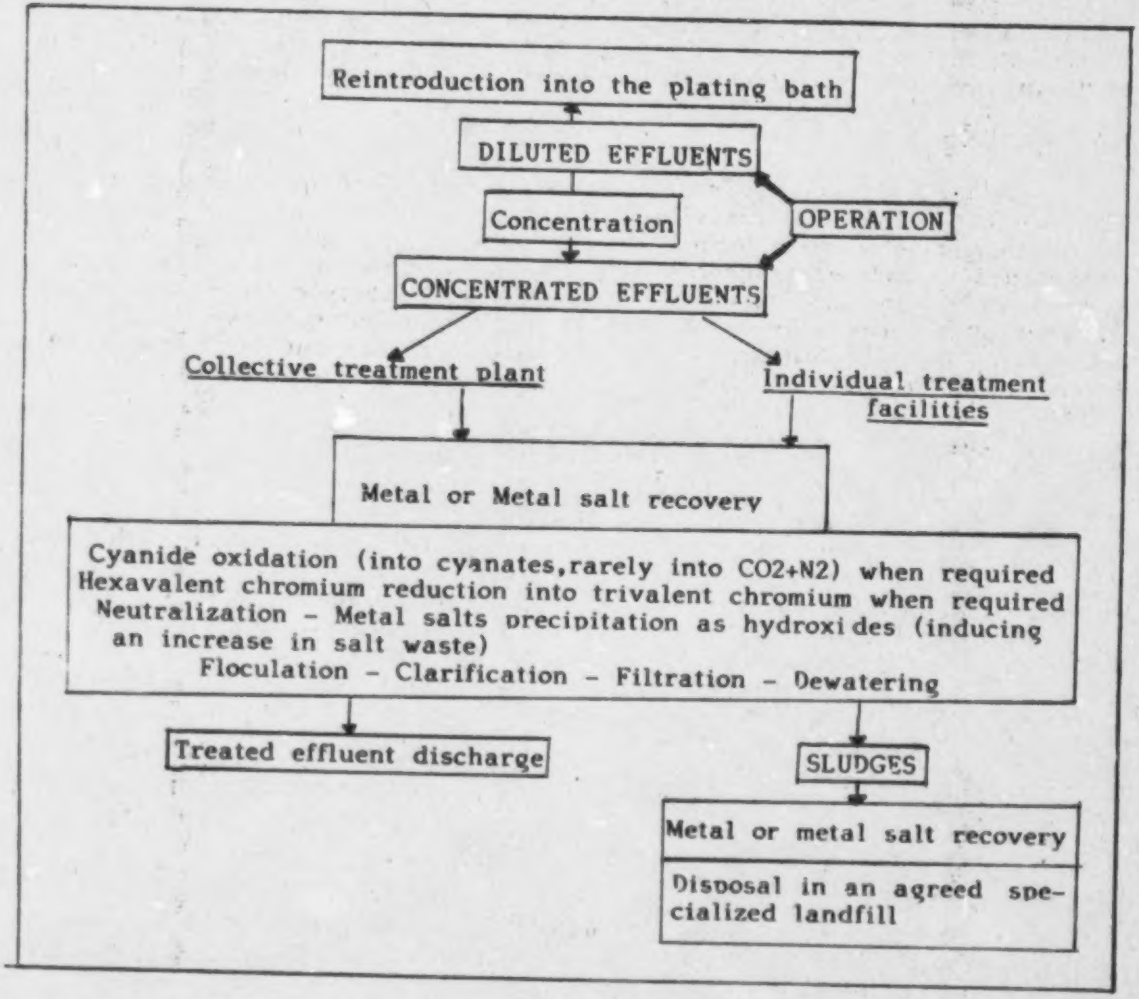
Recovery allows for valorizing metals which are contained in concentrated effluents mainly from spent plating baths. These metal salts come either from additives or from substrate etching.

The technical progress allows the recovery of most of the metals present in the effluents, but the main obstacles are the economics related to the recovery and the lack of marketing possibilities.

THE EFFLUENT TREATMENT :

In spite of the new juridical, administrative and financial provisions adopted in the various countries, the development of effluent treatments and, in a lower proportion, their efficiency, cannot be considered satisfactory. In fact, diluted or even concentrated effluents are too often discharged into receiving streams without undergoing the treatments required by the regulation in force.

THE FOLLOWING DIAGRAM SHOWS THE MAIN WASTE TREATMENT LINES :


Reintroduction into the plating bath
DILUTED EFFLUENTS
Concentration
OPERATION
CONCENTRATED EFFLUENTS
Collective treatment plant
Individual treatment facilities
Metal or Metal salt recovery
Cyanide oxidation (into cyanates,rarely into CO2+N2) when required
Hexavalent chromium reduction into trivalent chromium when required
Neutralization - Metal salts precipitation as hydroxides (inducing an increase in salt waste)
Floculation - Clarification - Filtration - Dewatering
Treated effluent discharge
SLUDGES
Metal or metal salt recovery
Disposal in an agreed specialized landfill

It can be observed that this treatment is rather a detoxification than a destruction of hazardous wastes.

In the case of diluted effluent treatment, the economic analysis shows that the item accounting for the highest investment is precisely the effluent concentration. This underlines the interest in limiting the volume of effluents to be treated by using effective techniques of control.

INTRODUCTION

PRESENTATION OF METAL FINISHING

The surface of any body, solid or liquid, may be defined by a group of :

- physical characteristics (structure, hardness, reflectivity, surface tension, etc...)
- chemical characteristics (chemical nature, pH, etc...)
- electrical characteristics (resistance, potential, etc...)

which represent the state of the surface of this body. Any effort to modify one or more of these characteristics implies an intervention which corresponds to the treatment of the surface under consideration.

From all possible surface treatments, we shall distinguish those which are used essentially to modify the following characteristics when applied to metals and alloys or plastics :

- corrosion resistance,
- hardening,
- improvement in appearence.

In the vast majority of cases, these methods of treatment make use of chemical or electro-chemical processes in a liquid medium and are applied to a large number of industrial productions.

The total sales were 9 billions Francs in France in 1974. In the United kingdom in 1975, 133,9 millions pounds relates only to contract plating by companies with more than 25 employees;

These processes cause substantial losses in toxic or costly products which become sources of pollution when disposed to the natural medium.

AMOUNT OF LOSSES

An estimation of losses is :

.60 to 80 % for chromic acid,

.100 % for cyanides of which 50 % are in liquid wastes and the rest are destroyed,

.5 to 10 % for metals (copper, nickel, zinc, cadmium ...),

.About 50 % of the acids, bases, salts...

In most cases, these losses are in the dissolved state, only some salts or hydroxides can be insoluble and are presented in the form of sludges.

The wastes taken into account in this study are therefore made of liquids of which the concentration in acids, bases, salts, metal and special additives varies from 10^{-3} to 10^{3} g/l. The waste is continuous throughout the operation of the activity or is discontinued during stoppages (daily, weekly, monthly or annual).

RESTRICTIONS ON THE POSSIBILITIES OF INTERVENTION

Two directions of intervention are possible :

- on the effluent producing lines : methods leading to a reduction in these losses and thereby achieving conservation of raw materials ;
- on the effluent treating lines : processes allowing for the recovery of valuable substances and for the elimination of wastes in conditions which are satisfactory for the environment.

While searching for these solutions, it is nevertheless necessary to take into account certain restrictions which are inherent in the structure itself of the profession :

- Surface treatment industries must be considered as manufacturing industries rather than as processing industries. They are heterogeneous with respect to the size of the various production units, types of products manufactured, types of use considered and the general technical competence of its executives. A large number of shops and factories apply electroplating in one form or another. Their location as well as the determination of necessary anti-pollution measures require considerable resources in time and in personnel. Attempts to combat pollution have been chiefly concentrated in large captive shops. The solution to the problem confronted by a large number of small shops remains difficult.

- Some investments shall be made for equipment which is not useful for obtaining the desired results. In fact, numerous shop managers, especially those having small production units, who do not have sufficient knowledge and experience to make sound choices among the various equipment for combating pollution, shall have to base decisions on sales arguments or on recommendations without considering specific facts relating to the problem under consideration.

- Personnel competence limits the complexity of equipment used in pollution control. Equipment which is easy to operate and maintain is therefore necessary, especially in small and medium-sized firms.

- Shops having a diversified production and utilizing diverse processes for electroplating, may have difficulty in the selection of equipment and operational conditions allowing for the various types of effluents to be treated with equal efficiency.

- Investments and the cost of operation for equipment appropriated for the treatment of effluents can exceed the financial capacity of small shops.

- The use of supplementary chemicals often having an unknown composition can interfere with effluent treatment operations in a manner which is difficult to define.

SCOPE OF CONTROL IMPLEMENTATION

Wastes generated by metal finishing come from :

- the substrates, i.e. the constituent substances of the work pieces (pickling, deoxidation, chemical or electrolytic machining) or from the substances of some deposits which should then be partially or completely eliminated (metal extraction, etching)

. mild and stainless steels
. copper and alloys
. aluminium and alloys
. other metals (nickel, chromium, zinc, titanium, etc...)

Except in the case of chemical machinings, the metal waste from the substrates represents a maximum of 2 to 3 % of the weight of the workpieces used.

- the product additions, i.e. products which are bought and applied to the treatment processes :

. acids, including chromic acid
. bases, including cyanide
. salts, including metal salts
. metal anodes (zinc, cadmium, copper, nickel, etc...)
. additives (brighteners, surface-active products chelating agents.

These are the essential waste products of metal finishing shops which we shall attempt to control.

The control of a substance loss means that an appropriate means is developed to prevent the product under consideration from being no longer serviceable, in its original state, in the sequences of plating operations.

Furthermore, metal losses during the pickling, deoxidation or machining processes proceeds from the decision to use the substrate for a given objective. Accordingly, this decision means that the metal extracted from the substrate must be considered a waste, as it is impossible to reintroduce it into the constituent substance of the workpiece.

The concept of control can, then, by no means be applied in the case of a waste originating from substrates ; only the concept of valuation can be applied for the recovery of metal wastes at the stage of "treatment" under consideration.

Hence, what we define as control, shall include all processes which allow for a reduction in the consumption, and thus the wastes, of a product addition, including metals, of course, for a given production. Recovered additives which are intended to be consumed or destroyed by 100 %, shall therefore be directly recycled into the treatment chain.

Furthermore, the techniques developed to control the most polluting wastes, most often result in substantial savings in the amount of water consumed.

The use of additives or technological variants can be related to control procedures. The application of waste free technologies involves the decision of modifying the nature itself of the treatment performed, therefore they are not control techniques.

Control must be distinguished from valuation, the aim of which is the recovery of additions or of the substrate consumed in a form which makes them useful for another application. This recovery is often administered at the stage of effluent purification. In some cases, however, the techniques applied shall allow for the control and valuation procedures to be combined. This is the case, for example, during the electrolysis of a copper pickling bath which controls the sulphuric acid wastes, as the copper deposited in the cathode is valuated by being reintroduced into the foundary.

CONTROL PROCEDURES

A well-researched utilization of the various rinsing techniques coupled with the ion exchange processes should suffice in most cases to ensure a quasi-total waste control. They are thus presented with special emphasis.

With respect to the evaporation and reverse osmosis processes, the new techniques proposed depend on chemical engineering and are applicable only in large plants. This explains why they are used very little ; for example, in France, the industry has not yet developed basic tools.

Even though they are accessible to small firms, the use of electrolysis and electrodialysis is still not wide spread.

The substitutions of cyanides, chromium and toxic or costly metals by non polluting products should be approached with caution, as these substitutions an in some cases create serious disadvantages. For example, cyanide is easily eliminated from effluents by destructive oxidization ; when it is substitued by a new chelating agent, the effect is often an increase of metal wastes in a soluble form.

THE EFFLUENT TREATMENT

The effluents are composed with :

- indestructible substances : metals or metal salts, fluorine , etc...
- components, the toxicity of which may be destroyed or more often reduced :
  - The cyanide ion CN^- which can become $CO_2 + N_2$ but which is usually oxidized into cyanate,
  - The hexavalent nature of chromium which can be reduced to the trivalent state,
  - The acid or base molecule which can be converted into salt + water,
  - The nitrite ion NO_2 which becomes $N_2 + O_2$.

In these conditions, the treatment of wastes produced in the surface treatment industry cannot be systematically assimilated into the destruction process, as can be the case for organic matter, as it is most often advisable to convey this concept of treatment by the following succession of states :

- Conditioning + transfer + discharging or direct waste,

and only in some cases by the succession of states :

- Destruction + supplementary salt waste,

the treatment quality being a function of the conditioning process and of the discharge site which shall have been selected.

It follows that the solutions to the pollution problem which have been applied in the metal finishing industry do not prove to be particularly practical, for either it is a case of conditioning which has a questionable efficiency, or it is a case of a destruction which is accompanied by a substantial supplementary addition of salinity.

It may be added that it is not very easy to carry out treatments with the tools currently available (pH meters and rH meters). These measurements are often inadequate, particularly during the evaluation of metal insolubilization when human intervention is indispensable for obtaining satisfactory results.

RECOMMENDATIONS

The effort to reduce pollution from metal finishing industry takes place at two levels :

- in priority, development of pollution control techniques,
- satisfactory treatment of wastes inevitably produced.

1 - DEVELOPMENT OF POLLUTION CONTROL TECHNIQUES

These techniques exist, but must be perfected and adapted to each case. In order to develop their use, it is necessary to change the methods and outlook of the manufacturers in question. Several types of measures may be recommended to this end.

a - Regulation pressure

Waste laws and executive enactments prescribe on metal finishing manufactures a lot of obligations which they feel as constraints. But regulation may be used as a pedagogic tool to urge manufacturers to employ less polluting processes and to increase their recycling and recovery potential. For example, these rules could encourage the establishment of registers in which all consumptions, flows, fluxes, discharges would be systematically noted.

Moreover, reglementation could allow for a clear identification of responsibilities within companies involved : precise designation of a "Waste Manager", within the company, with a sufficient level of responsibility, is a basic element for a detailed study of means to be used in the fight against pollution either at the waste pollution level or at the treatment level (clause 20 of the Belgium Waste Act of the 22th July of 1974 deals with the statute of a person responsible for waste treatment, as does German legislation). The waste manager must communicate directly with the authorities. Manufacturers would bear the cost of remuneration and training of the waste manager.

b - Training and information

The various "Waste managers" must be trained in new techniques. It is thus necessary :

- to disseminate detailed technical information documents,
- to develop specialized professional training in order to inform shop managers of practical aspects of handling of raw materials (setting up an input-ouput balance and an economic balance),
- to provide for standard guidelines.

c - Economic pressure

It is desirable to apply the "polluter-payers" principle, whereby pollution producers pay taxes or fees as a function of quantities consumed or discharged In order that measure be applicable, discharges standards must be related to a quantitative control system.

d - Applied research and consulting

Research for new simple technologies which can be easily used must be continued. The adaptation of these new technologies to cases must be encouraged. In this context, it appears whorthwhile to encourage the creation of a "technical centre" (or the creation of a division in an existing research organization which will be charged with these problems). The purpose of this organization would be, in addition to the development of loss control techniques, to technically aid industries and to organize the necessary training.

e - Recovery

Recovery which allows for marketing the main substances contained in operation residues is an important means to be used in fighting against pollution (and in saving raw materials). It is thus necessary to aid the creation of facilities specialized in recovery and to encourage those technologies that have significant impact on the potential for recovery.

It will always be necessary to remind people that it is inadvisable to mix different waste streams if recycling and recovery possibilities are to be improved.

2 - EFFLUENT AND SLUDGES TREATMENT

Regardless of the reason, wastes are produced which must be satisfactory treated by physico-chemical treatment after recovery in concentrated baths when possible.

A certain number of recommendations may be made to assure this treatement under the best possible conditions :

- It is recommended, especially for small capacity units, to engage the services of a specialized collective treatment centre or, where this is not possible, to use the facilities of greater units. This would assure a greater economic efficiency and, more important, greater safety enabling recovery solutions to be considered in so far as the various effluents or sludges are not mixed.

- In the case of individual industrial waste treatment facilities, an appropriate personnel training is necessary to ascertain a satisfactory operation of the station.

- In the case of liquid waste discharge to public sewage treatment plan, it should be ensured that the followings are respected :
  - no disturbance to the operation of the waste water treatment plant,
  - no contamination of the sludge issued from the waste water treatment plant,
  - no untolerable release into the environment.

- Temprary storage of sludges containing highly valuable materials for which recovery technologies could be developed during the next years, is a solution to encourage. However, this storage will have to be selective according to what the sludges contain, and will have to be carried out in satisfactory conditions with regard to the environment protection.

-1-

DESCRIPTION OF THE INDUSTRY AND ITS POLLUTION POTENTIALS

1.1. STRUCTURE OF THE INDUSTRY

1.1.1. In France

It is striking to observe that in all countries, the subgroup comprising the metal finishing industry is extremely difficult to describe as it appears to be relatively disorganized.

Normally, it is customary to distinguish captive shops from small job shops based on whether metal finishing is part of a larger production process, or whether it is the chief activity of a firm.

Whereas captive shops are classed by their main activity (aeronautics, automobile, telophone, furniture, metal, etc...) job metal finishers in France have a special title in the nomenclature of economic activities.

It should be pointed out that this distinction has become less accentuated over the past few years. The captive shops are in fact becoming extremely well-equipped and perform job shops operations generally with more efficiency than the job shops themselves.

Evaluations of the industry based on various cross-checkings have given the followings results :

The sales volume excluding taxes for the whole surface treatment industry expressed in 1974 Francs should amount to 9.13 billion francs of which 80 % is for the captive shops -the iron and steel industry plays a predominant role among them due to the high production of galvanized, tinned sheet iron- and 20 % for the job shops. The total labour force should be about 100,000 for the entire profession, including about 25 % for the metal finishing industry. There are about 2,300 job shops in France out of a total of 6,000 to 7,000.

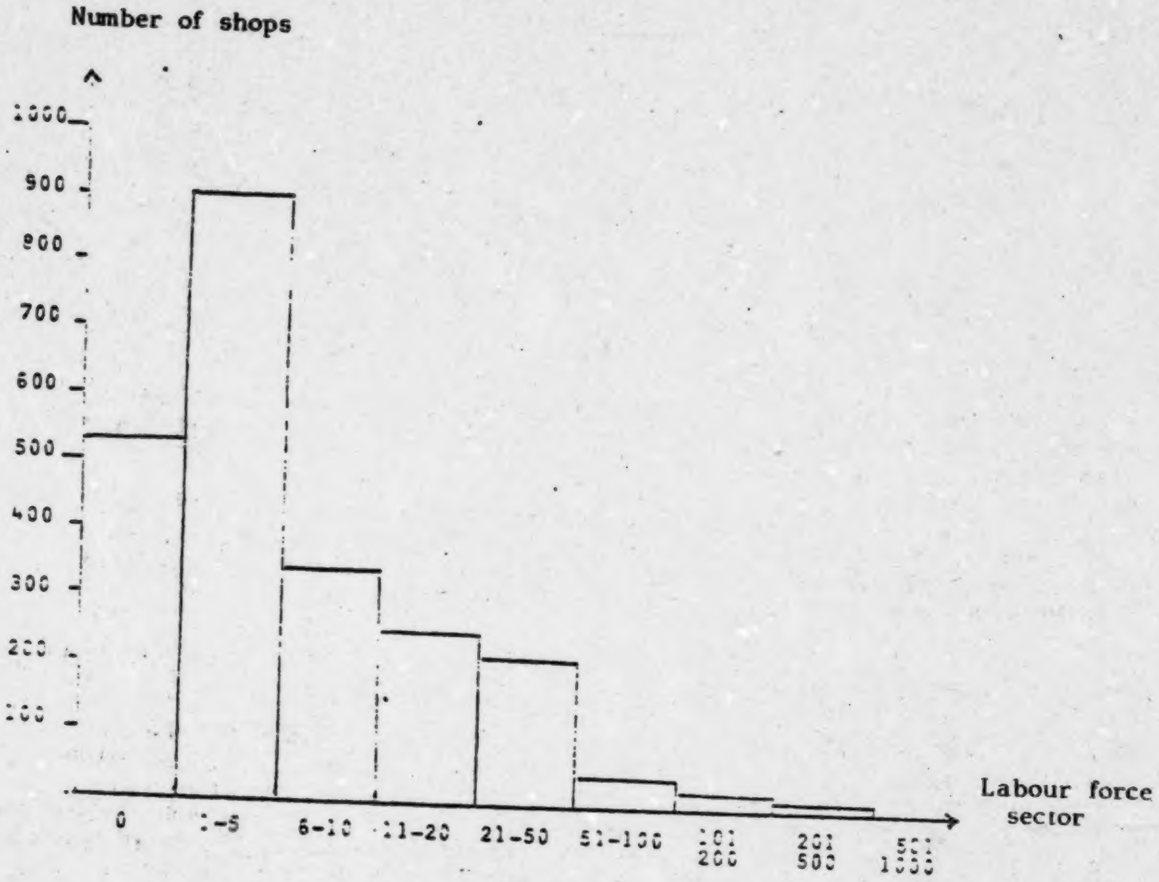


TABLE 1 :

Salaried workers by sector
(Number of shops for each labour force sector)

1- There are large numbers of shops without salaried workers (more than 500) : many are small arts and crafts shops where work is carried out in questionable technical conditions.

2- Most shops have a labour force between 1 and 5 (900).

3- No shop employs more than 500 workers.

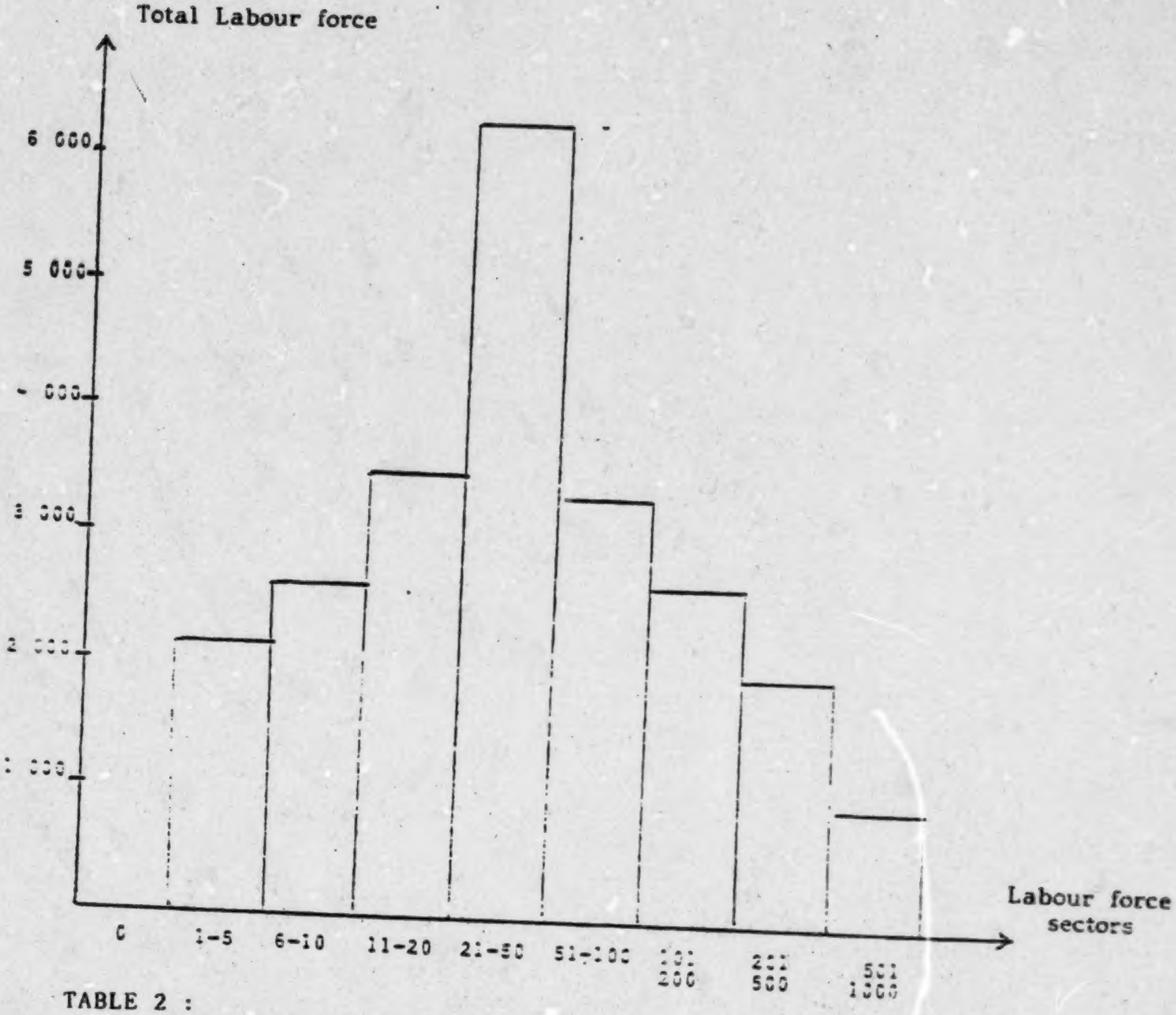


TABLE 2 :

Sectors of salaried workers
(Total labour force for each sector)

It may be observed on Table 2 that the shops employing from 21 to 50 salaried workers makes up the category with the largest number of workers (more than 6,000), but the average job shops employs about 10 workers.

For all metal finishing shops, whether they are captive or job shops, statistical analysis shows that there were on average 24 employees per shop..

It may further be pointed out that for the whole of the metal finishing industry, a distinction may be made between chemical treatments and galvanic treatments. They do not have the same unions nor the same standards for entering the profession.

METAL	CAPACITY	DISTRIBUTION captive shops - job shops
Zinc	2,600.000 liters	50 - 50
Nickel	3,500.000 liters	65 - 35
Chromium	1,200.000 liters	65 - 35
Copper	700.000 liters	65 - 35
Tin	130.000 liters	50 - 50
Cadmium	50.000 liters	60 - 40

TABLE 3 :
Capacity for electrolytic baths of common metals in France

With respect to precious metals, gold deposits are predominant. The electronics industry, which does not have job shops for these treatments, deposits some 300 kgs of gold per month. The decorative arts, which makes use of job shops for about 20 % of the works, deposits 200 kgs of gold per month approximately.

For chemical treatments, the capacity established in liters for baths is not very significant.

The automobile industry is equipped with a capacity of several million liters in chemical treatment tanks.

Electrochemical nickel plating	35 %
Chemical nickel plating	7 %
Electrochemical copper plating	26 %
Chemical copper plating	5 %
Zinc plating (chemical and electrochemical)	27 %
Cadmium plating (electrochemical)	18 %
Decorative chromium plating (electrochemical) and chromatizing	33 %
Thick chromium plating (electrochemical)	8 %
Copper pickling (chemical)	12 %
Steel pickling (chemical)	21 %
Stainless steel pickling (chemical)	8 %

TABLE 4 :
Plating distribution in the shops of the Rhone-Mediterranée Basin

TABLE 5 : DISTRIBUTION OF TOXIC FLUX IN BASINS

TOXIC FLUX / BASINS	ADOUR GARONNE	ARTOIS PICARDIE	LOIRE BRETAGNE	RHIN MEUSE	RHONE M. C.	SEINE NORMANDIE Without Paris area	SEINE NORMANDIE Within Paris area (1)
COPPER	1 %	5 %	17 %	11 %	30 %	16 %	20 %
NICKEL	3 %	4 %	11 %	2 %	11 %	15 %	54 %
CHROMIUM	6 %	10 %	19 %	12 %	10 %	24 %	19 %
ZINC	2 %	7 %	15 %	11 %	26 %	23 %	16 %
CADMIUM	6 %	1 %	18 %	5 %	10 %	31 %	29 %
CYANIDES	2 %	7 %	15 %	11 %	26 %	23 %	16 %
FLUORIDES FLUORHYDRIC ACID	6 %	ε	51 %	3%	5 %	17 %	18 %
COPPER PICKLING	ε	53 %	1 %	ε	17 %	22 %	7 %
STAINLESS STEEL PICKLING	1 %	ε	54 %	1 %	22 %	10 %	12 %
ALUMINIUM PICKLING	0 %	1 %	40 %	5 %	19 %	22 %	5 %
EVERY FLUX MIXED (2)	3 %	16 %	15 %	8 %	18 %	21 %	19 %
NUMBER OF SHOPS (3)	137	158	227	166	~ 320	~ 1200	

(1) The six departments : 78, 91, 92, 93, 94, 95

(2) A factor was assigned to each pollutant characterizing its inhibiting influence.

(3) Very small shops are not taken into consideration.

It appears that the tonnages sold annually in the profession are more significant.

The annual consumption is about 40,000 tons of chemicals ranging from degreasers to phosphate treatments by passing through rust removers, chromic passivants, chemical oxidations. Chemical treatments present particularly problems of neutralization in large volumes, but make use of very few real toxic products (cyanides are not used at all, for example).

1.1.2. In the United States

Three segments of activity are distinguished :

- the plating segment (chemical and electrochemical plating) operated in 10,000 companies included 3,400 job shops. An annual increment of 2 billion US $ for job shops and 10 billion US $ for captive shops is earned.

- the metal finishing segment (anodizing, dyeing...) operated in 15,000 companies.

- the printed board segment : 14 millions m^2/year distributed to :

. the domestic market : one billion US $

. the export market : 2 billion US $

More than 52 % of all electroplating and metal finishing esyablishments are located in cities having a population greater than 100,000 and more than three quarters of the plants are located in cities with a population greater than 20,000.

Labour distribution in the job shops is the following :

. 1 to 4 workers : 12 % of the shops
. 5 to 10 workers : 27 % of the shops
. 11 to 25 workers : 30 % of the shops
. 26 to 50 workers : 20 % of the shops
. 51 to 100 workers : 8 % of the shops
. 101 to 500 workers : 3 % of the shops

Out of a sample of 50 captive shops visited, the average labour force was 53 employees.

1.1.3. In the Netherlands

TREATMENT	TOTAL SALES1975 fl x 10^6	EMPLOYEES
Blasting	160	1 600
Pretreatment (chem. and phys.)	55	700
Plating	300	4 500
Anodization	45	700
Hot Dip galvanizing	90	1 200
Enamelling	25	400
Spraying (metal and flame)	25	450

TABLE 6 :
Total sales and number of employees in the metal finishing industries in 1975.

1.1.4. In the Federal Republic of Germany

The number of captive electroplating shops which are related to only about 400 larger companies is estimated to be 5,000 to 7,000 in addition to another 600-700 electroplating job shops.

According to other sources, the electroplating industry is estimated to take place in a total of 6,000 enterprises comprising 25, 000 employees.

The respective shops and firms are not organized in a single trade association but are represented in about twenty different associations.

The main regional centres of galvanotechnical industry are located in the following areas :

. In NorthRhine Westphalia region :

where there are 784 metal processing firm including only 130 (17 %) pure electroplating enterprises. These pure electroplating firms are in the majority small to medium size enterprises with 118 employers in average. 80 per cent of the enterprises employ less than 200 persons ;

. In Nortwürttemberg region :

where 19 % out of 300 metal processing firms are pure electroplating enterprises, 24 % steel and aluminium processing enterprises and 57 % mixed enterprises with electroplating captive shops.

A survey of 81 electroplating firms showed that 31 % of the enterprises (even 41 % in the section of electroplating job shops) are small firms with less than 10 employees.

A survey involving 185 metal processing firms in the country of Northwurttemberg indicated an amount of 19,200 tons of hydroxide sludge with an average water content of 72 %, i.e. about 100 tons per firm annually. In 50 % of theses enterprises only 26,4 tons per year are generated while in 2.4 % of the enterprises, more than 1,200 tons crop up.

In the metal finishing section, an extremely high proportion of small and very small firms is established with low degree of automatization and little inclination to specialize. These enterprises apply a wide range of different materials and processes. The very strength of these enterprises is born in their flexibility.

1.1.5. In Canada

There are more than 7,000 plants in Canada that can be broadly defined as metal finishing operations, but only 325 of them, a labour force of 7,000 employees are bound by the Federal Regulation. One half of these salaried employees work in captive shops. 90 % of that industry is located in Ontario and in Quebec.

Most of the production comes from captive or job shops employing more than 500 persons, but more than 200 companies employ less than 50 persons, including 100 companies employing less than 10 persons.

Most of the job shops belong to private owners who operate by themselves whereas captive shops are owned by large Canadian or United-States companies.

1.1.6. In the United Kingdom

A reliable estimate of the total number of general metal finishing installations is probably of the order of 3 000 to 4 000 units. There are about 40 to 50 specialist anodizing companies, although overall about 23o companies handle anodizing work. In galvanizing, there are about 30 to 40 specialist companies.

1 000 to 1 200 companies are contract finishers of whom perhaps two-thirds (750 companies approximately) employ less than 25 workers. Many units are very small, employing less than 10 people including the principals.

A total of 2 347 workers are employed in metal finishing companies of 25 people or less ; this total represents about one-third of the total number of workers employed in metal finishing.

Supporting evidence for this distribution can bededuced from an analysis of the volumes of effluent produced by metal finishing companies. The data shows that about two-thirds of the companies each produce less than 4.546 x 104 m3 (10 m.g.) of effluent per annum.

TABLE 7 :

RELATIVE IMPORTANCE OF METAL FINISHING PROCESSES IN THE UNITED KINDOM

PROCESS	VALUE OF WORK DONE* (£)	% OF TOTAL SALES
Anodising	8,2	6,2
Galvanising	11,8	8,9
Hot Dip Coating (other than galvanising)	7,6	5,8
Electroplating		
Hard chrome	7,2	5,5
Decorative chrome (1)	11,1	8,4
Nickel	3,9	3,0
Precious metal	3,8	2,9
Zinc, cadmium and tin	10,7	8,1
Other	2,2	1,7
TOTAL ELECTROPLATING	38,9	29,6
Vitreous Enamelling	2,6	2,0
Japanning, Lacquering or Stove painting	3,8	2,9
Metal Spraying	6,2	4,7
Other Metal Finishing (2)	43,8	32,9
	122,9	
Other work done	9,2	7,0
Total value of metal finishing work	132,1	100,0
Miscellaneous (3)	1,8	
Total sales and work done by establihments classified to MLH 399.11 (Metal finishing)	133,9	

NOTES :

(1) : Includes copper-nickel-chromium plating.

(2) : Mainly chemical treatments.

(3) : Includes revenue from waste products and residues sold, services rendered to other organisation, etc.

* : Net selling values : VAT, trade discounts and commissions are excluded. Values given relate to 1975.

1.2. CONSUMPTION OF RAW MATERIALS AND DISCHARGE OF POLLUTANTS

The biggest polluters are eletrolytic treatments which make up 85 to 90 % of the total discharged pollutant flow. In spite of the large volumes of baths involved, chemical surface treatments represent only 10 to 15 % of the total discharged pollutant flow.

Considerable quantities of wastes are disposed of :

- In the United States, the disposable wastes produced by the surface treatment shops are expected to double in 8 years because of waste water pretreatment requirements.

Disposable sludges and solid wastes (T/year) :

	Job shops	Captive shops
1975	79,000	830,000
1977	115,000	1,200,000
1983	151,000	1,600,000

- In Germany, it is estimated that the amount of hydroxide sludges produced exceeds 200,000 t/y, or an average of 100 to 200 t/y per firm for sludges containing 60 to 80 % water.

- In the United Kingdom, the production of effluents and of liquid wastes is close to $1.8 \times 10.^{6}$ m3/y, whereas sludges and solid waste mixtures represent 10^{5} t/y.

The comparison of the consumptions of additives brings to light similar figures for countries with a similar industrial potential. Accordingly, we may assume that these figures appear to be consistent. The essential question, however, is to know the percentage of polluting substances discharged into the effluents, whether it is a case of waste waters from baths or from rinsing. The waste coefficients, however, are extremely difficult to define because of their uncertain characteristics and because of considerable variations between firms. Here again, it appears that the situation is very similar in the various countries consulted, and particularly that the discharge of wastes of the metal finishing industry is a major problem, both from the point of view of pollution caused and from the point of view of raw material wastes.

An important factor which should be considered is the form in which these wastes appear, i.e. a distinction should be established between:

- spent baths which usually are low in volume, but have a high content in polluting materials,
- highly diluted rinsing water which is usually high in volume,
- metal hydroxide sludges resulting from the treatment of effluents.

It is very difficult to provide correct data on these different aspects.

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TABLE 8 : CONSUMPTION OF RAW MATERIALS (*) (TONS DRY MATTER PER ANNUM)

ADDITIVES	NETHERLANDS (1975)	F. R. G. 1977	F. R. G. 1978	UNITED KINGDOM 1975	FRANCE 1974	CANADA 1975
Cadmium	3	365	365	400	350	70
Chromium (as CrO3)	170	2 500	2 625	2 500	2 500	500-700
Copper		3 000-4 000	3150-4200	2 000-2 500	2 500	250
Nickel	160	5 500	5 500	3 500-4 000	4 000	3 000
Zinc						
- plating	30	7 000-9 000	8 000-10000	7 000-8 000	5 000	300
- galvanizing				75 000	80 000	
Tin		5 000	5 250	1 000	3 000	20
Cyanides						
-electroplating	30	500	400	2 000 à 2 500	3 000	600
- heat treatment	20			2 000		
Fluorides	40			900	900	
Hcl pickling plating	1 800			7 500		10 000
galvanizing	20 000			7 500		
HNO3	300			2 500		
H2 SO4 galvanizing	1 200			7 500		
misceallaneous				1 500		
H3 PO4	360			4 500		1 500
Na OH				7 500		1 100

(*) Criteria for consumption evaluation seem not to have been the same in the various countries.

TABLE 9 : YEARLY CONSUMPTION IN THE NETHERLANDS IN TONS/ANNUM (basis 1971)

composed of	cleaning and degreasing	Hot Dip galvanizing	pickling etching and shining	plating	converting	TOTAL
Chromium	3		50	420	60	530
nickel				400		400
zinc		10000		40		10040
cadmium				3		3
cyanide (*)	60			270		330
Fluoride			30	8	2	40

(*) excluding hardening salts.

Chromium as : dichromates, chromic acid, chromiumsulfate, etc...

Nickel as : - chloride, - sulfate, - sulfamate.

Zinc as : - cyanide, - nitrate, - oxide (thermal zinckling : metal).

Cadmium as : - cyanide, oxide, - fluoborate.

Cyanide as : - potassium - and sodium -, copper - and zinc -

Fluoride as : - fluoborates, - difluorides.

NATURE OF THE DISCHARGE	Tons/annum (dry matter)
sludges from steel pickling	2,300
sludges from zinc pickling	20
sludges of nickel hydroxide	160
sludge of chromium hydroxide	200
lead chromate precipitate	35
chromium hydroxide from chromatizing	10
$Cr_2 (CO_3)$ sludges from zinc plating	65
cadmium hydroxide	0.6
chromatizing spent bath sludges containing Zn, Cd	4.4
hardening salts, as Na CN and Ba Cl_2	100

TABLE 10 : DISCHARGES IN THE NETHERLANDS (1971)

ADDITIVES	UNITED KINGDOM		F.R.G.		FRANCE					
	Discharge T/year	disch. % consum.	Discharge t/year	Disch % consum.	Discharge t/year	Disch.% Consum.	Concentrated effluents T/year	Concentrated effluents g/l	diluted effluents t/year	diluted effluents g/l
Cadmium	4 à 20	1 à 5	18 à 91	5 à 25	20	6	5	40	15	30
Chromium (as Cr03)	1250- 1800	50 à 70	1575- 2500	60 à 95	1 800	70	300	40	1 500	35
Copper	40 à 200	2 à 10	150 à1250	5 à 30	200	8	20	40	180	20
Nickel	100 à 400	3 à 12	165 à 1100	3 à 20	225	6	60	25	200	25
Zinc' (electroplating)	200 à 800	2 à 12	800 à 3000	10 à 30	260	6	60	25	220	15
Cyanides					1 500	50	250	25	1 250	25
Fluorides					750	85	150		600	
SUBSTRATE (pickling)										
Copper					150	1,2 ‰			150	
Aluminium					100	1 ‰	10		90	
Stainless steel					300	1 ‰			270	

100 % of bases and acids are discharged. Weights sum up recovered materials

TABLE 11 : DISCHARGE IN THE UNITED KINGDOM (1975), in F.R.G. (1978) and in FRANCE (1974)

TABLE 12 : COMPOSITION AND PROPERTIES OF SOME SLUDGE SAMPLES FROM THE UNITED KINGDOM

Processes	Non ferrous Pickling	Metal finishing	Plating	Nickel and chromium plating	Nickel and chromium plating
Neutralisation Alkali	Sodium hydroxide	calcium hydroxide	calcium hydroxide	Sodium hydroxide	calcium hydroxyde
Sludge : DESCRIPTION	blue flocculent	Greyish-green	Graenish grey	Reddish brown	light-kaki green
Ph	9,2	9,6	7,4	9,5	8,5
Calcium % on suspended solids	1,5	17,5	14,5	11,2	21,4
Cadmium " " "	0,005	-	0,03	-	-
Chromium " " "	0,004	1,6	7,5	2,3	7,0
Copper " " "	28,0	4,6	0,01	0,3	0,2
Iron " " "	-	0,8	2,5	19,0	2,4
Lead " " "	1,9	0,1	0,06	0,04	0,05
Nickel " " "	0,03	1,1	5,8	6,8	4,8
Zinc " " "	22,1	5,8	2,0	0,07	0,05
FILTRATION DATA					
Specific resistance to filtration of sludges in sec.^{2}g^{-1} (at 10 p.s.i.)	$8,4 \times 10^{8}$	$2,7 \times 10^{8}$	$4,7 \times 10^{8}$	$7,8 \times 10^{8}$	$3,8 \times 10^{8}$
% SOLIDS SLUDGE	1,9	2,6	4,7	2,3	6,7
% FILTER CAKE	sludge not filtered	27,6	29,5	sludge not filtered	42,2

TABLE 13 : AVERAGE COMPOSITION OF ELECTROLYTIC SLUDGES FROM THE U.S.A.

METAL	Percentage of dry matter	Substance	Percentage of dry matter
Copper	8,0	$Cu(OH)_2$	12,3
Chromium	7,5	$Cr(OH)_3$	14,8
Nickel	21,0	$Ni(OH)_2$	39,1
Zinc	11,0	$Zn(OH)_2$	17,1
Cadmium	1,0	$Cd(OH)_2$	1,7
Non metalleous	51,5	impureties	15,0

TABLE 14 : AVERAGE COMPOSITION OF 205 METAL FINISHING SLUDGE SAMPLES FROM NORTHWURTTEMBERG (in per cent by weight of dry matter)

Iron	8.9 %
Copper	1.7 %
Nickel	1.6 %
Chromium	3.3. %
Zinc	8.9 %
Cadmium	0.04 %
Lead	0.44 %
Mineral oil	1.4 %
Phosphate	9.7 %
Calcium	7.0 %

Additional constituents of the precipitation sludges may be solvents or detergents. Often in effluents of metal finishing, complexing reagents occur, such as ammonia and E D T A, which can limit the efficiency of hydroxide precipitation.

Only 39 % of the generated sludges has a high content in non-ferrous metals, while the rest is rather rich in iron and alumina.

waste waters from metal finishing
Control 1970, 270)

Type of liquid	Relative Importance (see note 1)	Components
2)		
	3	Paraffin, white spirit, trichlorethylene
esers	3	Kerosene, white spirit, emulsifying agents
	2	Hot emulsions of kerosene type solvent (2–20 per cent) in water
	1	Sodium metasilicates, pyrophosphates, carbonates, inhibitors, surfactants
ers	3,4	Hot solutions of mixtures of amines, soaps and emulsifiers
	2,3	Sulphuric, hydrochloric and phosphoric acids, phosphoric/hydrochloric acid mixtures, alkaline derusting salts (caustic soda, gluconates, heptonates, sodium cyanide)
	4	Nitric/hydrofluoric acid mixtures
ys	3,4	Sulphuric acid, mixtures of sulphuric and nitric acid plus accelerators, mixtures of chromic and sulphuric acids, sodium cyanide, sodium dichromate
	2,3	Sulphuric acid, nitric acid, hydrofluoric acid, sulphuric/hydrofluoric acid mixtures, caustic soda
	5	Sulphuric acid, nitric acid
ions		Sodium carbonate, metasilicates, borates, phosphates, chromate, cyanide, soaps, surfactants, sequestering agents, rust inhibitors, tartrates, ammonium salts, anti-tarnishing agents
cal		Mixtures of concentrated phosphoric, sulphuric and chromic acid, sometimes glycerine and aniline, also nitric/phosphoric/acetic acids from bright polishing before anodizing

Type of liquid	Relative Importance (see note 1)	Components
Desmutting solutions	5	Nitric acid, chromic/phosphoric acid mixture, caustic soda, ferric sulphate
Passivating solutions	3	Sulphuric acid and sodium dichromate, nitric acid
Alkaline cleaning solutions	1	Hot solutions of alkaline salts, surfactants, sodium cyanide
Plating solutions		
Cyanide-based	1	Copper, zinc, cadmium, silver, brass, bronze and tin/zinc cyanides
Acidic	1	Sulphuric acid; copper, zinc, nickel, tin sulphates and zinc chloride
Fluoborate-based	5	Cadmium, copper, lead, nickel, tin, zinc, fluoborates
Pyrophosphate-based (for copper)	5	Pyrophosphate, copper
For electroless plating	3,4	Alkali, silver, copper, nickel, phosphite, formaldehyde, hydrazine, tartrate
For tin	4	Sodium or potassium stannate
For nickel	1	Nickel, sulphamates, borate, silicate
For chromium	2	Chromic acid
Miscellaneous		
Rinse waters and dragout	1	
Bright dipping solution	4	Dilute nitric or sulphuric acid, sometimes containing chromate
Aluminium anodizing solution	2,3	Sulphuric acid, chromic acid, oxalic acid
Anodizing process effluents		Aluminium hydroxide (in suspension as well as in solution)
Dyeing solutions for anodized components	3,4	Ferric ammonium oxalate, cobalt acetate, potassium permanganate, organic dyestuffs, nickel or cobalt sulphates
Stripping residues		Sulphuric, hydrochloric, nitric and chromic acids, ammonium nitrate, sodium cyanide, sodium hydroxide, cresols, phenols, benzene sulphonates, basic metal sludges etc

Notes 1: 1 = maximum, 5 = least important (based on experience in electroplating industry)
2: These wastes were not considered by the Sub-Group.

TABLE 15

Types of solutions and waste waters from metal finishing (from W Lowe, Wat. Poll. Control 1970, 270)

Type of liquid	Relative Importance (see note 1)	Components
Degreasing agents (note 2)		
Solvent degreasers	3	Paraffin, white spirit, trichlorethylene
Emulsifiable solvent degreasers	3	Kerosene, white spirit, emulsifying agents
Emulsion cleaners	2	Hot emulsions of kerosene type solvent (2–20 per cent) in water
Alkaline spray cleaners	1	Sodium metasilicates, pyrophosphates, carbonates, inhibitors, surfactants
Aqueous organic precleaners	3,4	Hot solutions of mixtures of amines, soaps and emulsifiers
Pickling solutions		
For iron and steel (note 2)	2,3	Sulphuric, hydrochloric and phosphoric acids, phosphoric/hydrochloric acid mixtures, alkaline derusting salts (caustic soda, gluconates, heptonates, sodium cyanide)
For stainless steel (note 2)	4	Nitric/hydrofluoric acid mixtures
For copper and copper alloys	3,4	Sulphuric acid, mixtures of sulphuric and nitric acid plus accelerators, mixtures of chromic and sulphuric acids, sodium cyanide, sodium dichromate
For aluminium and alloys	2,3	Sulphuric acid, nitric acid, hydrofluoric acid, sulphuric/hydrofluoric acid mixtures, caustic soda
For magnesium and alloys	5	Sulphuric acid, nitric acid
Mechanical polishing solutions		Sodium carbonate, metasilicates, borates, phosphates, chromate, cyanide, soaps, surfactants, sequestering agents, rust inhibitors, tartrates, ammonium salts, anti-tarnishing agents
Chemical and electrochemical brightening and polishing solutions		Mixtures of concentrated phosphoric, sulphuric and chromic acid, sometimes glycerine and aniline, also nitric/phosphoric/acetic acids from bright polishing before anodizing
Desmutting solutions	5	Nitric acid, chrom caustic soda, ferr
Passivating solutions	3	Sulphuric acid an nitric acid
Alkaline cleaning solutions	1	Hot solutions of sodium cyanide
Plating solutions		
Cyanide-based	1	Copper, zinc, cadn bronze and tin/zin
Acidic	1	Sulphuric acid ; co tin sulphates and z
Fluoborate-based	5	Cadmium, copper, fluoborates
Pyrophosphate-based (for copper)	5	Pyrophosphate, co
For electroless plating	3,4	Alkali, silver, coppe formaldehyde, hydr
For tin	4	Sodium or potassiu
For nickel	1	Nickel, sulphamate
For chromium	2	Chromic acid
Miscellaneous		
Rinse waters and dragout	1	
Bright dipping solution	4	Dilute nitric or sulph containing chromate
Aluminium anodizing solution	2,3	Sulphuric acid, chro
Anodizing process effluents		Aluminium hydroxid well as in solution);
Dyeing solutions for anodized components	3,4	Ferric ammonium ox potassium permanga nickel or cobalt sulph
Stripping residues		Sulphuric, hydroch acids, ammonium nit sodium hydroxide, c sulphonates, basic m

Notes 1: 1 = maximum, 5 = least important (based on experience in
2: These wastes were not considered by the Sub-Group.

CONTROL

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2.1. THE SEQUENCES OF PLATING OPERATIONS

Sequences of plating operations are numerous and various, more especially as a great number of combinations is possible, each one being designed in function of :

- the nature of the substrate,

- the characteristics required for the finished product and the conditions under which it will be used.

- the treatment type of workpieces(in the frame when their dimensions and their shape enable it without a considerable handling, or in the drum for small pieces,the latter treatment type involving more losses than the former),

- many factors peculiar to each shop (profitability criteria , available area, personnel efficiency, automatic working expansion...).

Even if low polluting technical variants are sometimes available, it can be foreseen that standard sequences will still have to operate for a long time, including the most polluting ones. This underlines the importance, while searching for waste free substitution techniques, to amplify control techniques which allow for optimizing the consumption rate of additives and limiting discharges.

The example on the next page shows the complexity of the sequences of plating operations.

2.1.1. Nature of the treatment

The extent of control will vary with the processes applied to achieve the objectives sought by metal finishing. These processes make use of one of the following methods :

2.1.1.1. Deposition on the surface of the substrate, a different kind of metal having the desired characteristics.

The deposition may be achieved by a chemical or electrochemical way. This second process has a wider extent, as table 4 in chapter 1 shows, and is particularly polluting : the baths are often cyanided ones, more concentrated in metal salts and usually more susceptible to impureties than the electroless plating baths.

For the sequences of plating operations, the implementation of procedures to control the losses of additives is always advisable. They permit a decrease in the consumption of metals, cyanides and chromic acid in conditions which are economically advantageous as compared to the cost of the purification processes.

EXAMPLE OF A SEQUENCE OF PLATING OPERATIONS

COPPER-NICKEL-CHROMIUM PLATING CHAIN

This series is used on substrates such as zamac, copper alloys (brass...), steel and ensures impact strenth, resistance to wear and to corrosion and creates an esthetic effect (for example upon car bumpers...)

A model for this sequence is the following one :

1. Chemical degrease
2. Rinse
3. Electrolytical degrease
4. Rinse
5. Acid cleaning
6. Rinse
7. Cyanided copper plating
8. Rinse
9. Acid cleaning
10. Rinse
11. Acid copper plating
12. Rinse
13. Acid cleaning
14. Rinse
15. Nickel plating
16. Rinse
17. Chromium plating
18. Rinse

The term "rinse" designates the rinsing function and envolves several tanks.

Any technological variants :

Only one acid rinse may sometimes substitute for stations 9 and 10.

Stations 13 and 14 are not required in every cases.

In the case of a zamac substrate, an ultra-sound degrease is often added to station 1, stations 9 to 14 are commonly suppressed, such as stations 17 and 18 in the case of zamac plated in the drum.

In the case of steel substrates, or of any copper alloys substrate, the use of a cyanided copper plating bath may be avoided by substituting the following series for stations 5 to 8 :

5 : Pickling
6 : Rinse
7 :Nickel plating
8 : Rinse

2.1.1.2. Etching or physico-chemical modification of the surface.

In this case, the metal present in spent baths or rinse waters comes from the substrate. Hence, the control procedure which only considers additive losses, is not applicable. The chemical agents are mainly acids and bases which are more or less concentrated and for which a final neutralization is usually more economical than loss control procedures.

However, some agents, chromic acid for example, should be recovered and recycled. Moreover, recovering the substrate metal allows for their valuation (electrolysis of copper pickling spent baths for example).

Tables 16 and 17 present these baths. A more detailed study of each bath is presented in Annex A.

2.1.2. Origin of losses

A summary input output balance for each sequence shows that the origins of losses are always the following :

- spent baths,
- rinses,
- evaporation.

The relative importance of these items can vary from one sequence to another and from one shop to another. However, some constants may be underlined.

2.1.2.1. Spent baths, losses due to maintenance

Spent baths are concentrated effluents, whose contents in miscellaneous salts vary from some grams to a few hundred grams per liter, but whose volume is relatively small.

Some progress, achieved in recent years, allows the lenghtening of the life of plating baths or lowering their concentration ; thus the amount of pollutants discharged with spent baths is reduced. Moreover, the life of baths may often be lenghtening by a continuous purification. These two procedures of loss control are not at all in concurrence, but they are complementary.

2.1.2.2. Rinses

Rinses are required after most plating baths because piece emergence drag out amounts of a solution having the same constituency as the bath and whose transfer into the next bath would be harmful.

Waste rinse waters are diluted effluents whose contents in miscellaneous salts vary from some milligrams to a few hundred milligrams per liter, but whose total amount is thousands of times higher than that of the spent baths.

TABLE 16 : METAL DEPOSITS

BATH	ROLE	AIM	APPLICATION	MAIN COMPONENTS	ADDITIONAL AGENTS	CAUSE OF DISCHARGE	NATURE OF TREATMENT
Copper plating	Preparation for subsequent treatments anti-corrosion protection electro forming decoration	Copper deposit	Metals Plastics	Cu + acids Cu + alkalines + CN	Brighteners Surfactants Organic products	No discharge maintened continuously by selective precipitation or selective electrolysis	Electrochemical or Electroless
Nickel plating		Nickel deposit	Metals Plastics	Ni + acids Ni + alkalines	idem		Electrochemical or Electroless
Chromium plating	anti-corrosion decoration hardening	Chromium deposit	Metals Plastics	Cr + acids	idem		Electrochemical
Zinc plating	Preparation for subsequent treatments Anti-corrosion Protection	Zinc deposit	Metals	Zn + acids Zn + alkalines Zn + cyanides	idem		Electrochemical or Electroless
Cadmium plating		Cadmium deposit	Metals	Cd + cyanides Cd + acids	idem		Electrochemical

TABLE 17 : ETCHING OR PHYSICO-CHEMICAL MODIFICATION OF THE SUBSTRATE

BATH	ROLE	AIM	APPLICATION	MAIN COMPONENTS	ADDITIONAL AGENTS	CAUSE OF DISCHARGE	TYPE OF TREATMENT
Pickling	Elimination of oxids stripping the metal	Pickling	all metals and plastics (dyeing)	Acids Alkalines	surfactants	Polluted by metals	Electrochemical or chemical
Oxydizing	Anticorrosion protection Preparation before painting	formation of oxidized metal coat	aluminium steel	Acids Chromium		Polluted by metals degradation of components	Electrochemical or chemical
Passivation	Quality improvement of deposit	Chemical modification of the surface	All metals	Acids Alkalines Chromium	organic products	Polluted by metals	Electrochemical or chemical

There are two standard designs for these techniques :

- Running rinses : the input flow of pure water is equal to the output flow of polluted water . Contents in chemical agents in such a rinse bath are theoretically constant ;

- Dead or Still or Recovery rinses : which grow richer with chemical agents up to a concentration decided upon by the desired efficiency of rinsing.

Rinse waste waters may be concentrated and eventually purificated to allow their reintroduction into the plating bath. In the case of a hot plating bath (40 to 70° C), waters from a dead rinse or from the first bath of a counter current cascade rinse may be used to balance the plating bath, compensating evaporation losses.

2.1.2.3. Evaporation

Vapors issued from hot plating baths are usually not considered as a cause of additive losses. However, in some cases, when the cathodic yield is bad, the reaction of electrolytic deposit works with a strong gas release which causes liquid, having the same characteristics as the plating bath, to be dragged out.

Vapors, for example charged with chromic acid, must be condensated and recycled into the plating bath. Moreover, this condensation may supply at least part of the energy required to concentrate rinse water by evaporation.

2.2. CONTROL PROCEDURES

2.2.1. Control processes

Economical and technical impact of these processes are detailed in Annex B. Informations on cost prices of these processes are presented in appendix of this Annex.

All the processes of additive loss control have common advantages, especially :

- Saving raw products,
- Decrease in the volume of sludges produced by the effluent treatment,
- Decrease in the consumption of reagents for effluent treatment,
- Decrease in rinse water consumption,
- Decrease in the size of effluent treatment facilities,
- Decrease in the salinity discharged after effluent treatment.

Some disadvantages are common to all the processes :

. New equipment has to be set up. The size of initial investment depends on the processes and flows to be treated, but taking into consideration the advantages mentioned earlier, there will often be a quick return.

. Increase in plant floor space required (retention, anti-acid lining).

2.2.1.1. Straining

The volume of solution dragged out on the surface of a piece is reduced by straining off the piece above the given solution prior to its transfer into the rinse.

Straining is recommended after any plating bath but optimization can only be designed through automatization. The straining time will have a technical limit determined by the drying of products dragged out at the hot bath oulet or by the occurence of the surface chemical reaction which is against the desired objective.

Specific disadvantages of straining are :

- Time increase in plating operation,
- Increase in handling to maintain productivity,
- Impact upon the design of sequence of plating operations.

2.2.1.2. Static recovery rinse

After a hot working treatment bath, one or several static rinses are arranged in a simple cascade to allow for the solution transfer from one bath to another. The solution coming from the first bath serves to compensate volume losses from the plating bath.

Specific disadvantages of this process are :

- Time increase in plating operations by increase in number of rinse tanks,
- Increase in handling to maintain productivity.

Specific advantages are :

- Decrease in labour for bath maintenance,
- Improvement of maintenance techniques of concentrated baths.

2.2.1.3. ECO rinse

ECO rinses are static rinses in which the piecesare immersed before and after the plating bath, without an intermediary running rinse.

Advantages and disadvantages are the same as for static recovery rinses, but the effect on the design of the sequence of platingoperations is more significant.

2.2.1.4. Ion exchange

Ion exchange may be used for two reasons :

- Regeneration of solutions by fixation of metal pollutants on ion exchange resins to prevent discharge,
- Recycling of a dragged out loss by fixation and concentration on ion exchange resins.

This process is favourable whatever the shop dimensions be.

The only disadvantage is operation relating to new equipment.

2.2.1.5. Evaporation

Theorically, concentration of rinse waters by evaporation and reintroduction into the plating bath permits the elimination of losses dragged out from a hot bath and allows for working in a closed circuit water + products.

A specific advantage of this process is decrease in labour by improving maintenance technique of concentrated baths.

Disadvantages are :

- Time increase in the plating operation by increase in the number of rinse tanks,
- Increase in handling to maintain productivity,
- Operation relating to new equipment.

Investment and operation costs are rather high, moreover this process is related to chemical engineering, therefore, it is reserved for large factories.

2.2.1.6. Reverse osmosis

Reverse osmosis allows for purifying the concentration of rinse waters, especially after nickel plating.

The advantage is an improvement in maintenance technique of concentrated baths.

The main disadvantages of this process, which is related to chemical engineering, as is evaporation, are :

- those relating to membrane fatigue,
- operation relating to new equipment.

This process is reserved for large factories because its application requires a high technical competency.

2.2.1.7. Electrolysis

Electrolysis allows the recovery in a metal form, of metal from additives (and eventually from the substrate). These metals will be able to be reintroduced into the plating bath as anodes.

The disadvantage of electrolysis is operation relating to new equipment, but this technique is well known to the manufacturer and should be advantageous whatever the dimensions of the shop .

2.2.1.8. Electrodialysis

Electrodialysis uses electrolysis effects, ion-exchange membrane properties and osmotic phenomena. It is specifically adapted to chromic solution purification and/or concentration.

The specific advantage of this process is a decrease in operating costs of the station under consideration and the valuation of recovered products.

The disadvantage is operating new equipment and particularly, in some cases, a modification of bath working.

This process, although it is rarely used, may be used whatever the shop dimensions.

2.2.1.9. Interrelations between the various techniques

Some tehniques are necessarily induced by the application of another one (Refer to the study of sequences of plating operations in Annex A.)

In the case of decorative chromium, for example, the application of electrodialysis on a static rinse induces a second control technique : evaporation to concentrate the chromic acid issued from the electrodialyser and to enable its reintroduction into the chromium plating bath. Inversely, evaporator induces cascade static rinses and purification of the chromic solution by ion exchanges.

2.2.2. Low or non polluting techniques

Technical variants for each plating bath (refer Annex A), allow for reducing the volume, the concentration or the toxicity of effluents, when their application is compatible with quality requirements (see, for example, the sequences of plating operations (2.1.) : substitution of nickel plating for cyanided copper upon steel substrate).

As for waste-free techniques (refer Annex A), vacuum metallization for example, they envolve an intervention on the nature itself of the treatment performed. This decision will have direct consequences on effluent production as these processes prevent discharge relating to chromium plating or other electroplating baths. But the effort required to operate these new techniques is often dissuasive to standards shops, therefore these techniques are usually reserved to new implantations.

- 3 -

TREATMENT OF EFFLUENTS

3.1. TREATMEMENT OF EFFLUENTS

(Refer to "The treatment of effluents in the various countries", item 4.2)

3.1.1. Treatments lines

Two types of effluents are to be distinguished :

. The diluted effluents : a large volume produced continuously (rinse waste waters),

. The concentrated effluents, the volume of which is much lower, and the production of which is intermittent (spent baths, maintenance).

3.1.1.1. The diluted effluents

Most of the rinse waste waters are discharged to the natural medium (for example, 95 % in the U.S.A.). They are summarily neutralized by mixing acid and alkaline effluents before discharging.

For the effluents having the highest contents in toxic substances (5 % in the U.S.A.), cyanides should be removed (oxidation of cyanides into cyanates, most often by hypochlorites) or hexavalent chromium should be removed (hexavalent chromium is reduced into trivalent chromium by bisulfites, sulphur dioxide or ferrous sulphate). Then the effluents should be neutralized by addition of soda or lime to a pH of 8 to 9 commonly, which enables metals to settle as hydroxides. The effluents are then either discharged to sewer, or clarified. The sludges from clarification are guided to the same line as the sludges from concentrated effluents treatment. When purificated waters are discharged, end-of-pipe treatment is involved and in the case of in-line treatment technology, when purificated waters are recycled into rinses, then this concerns close loop treatment.

Another procedure consists in concentrating diluated effluents (mainly by ion exchange) which should then be treated with the concentrated effluents. This procedure is especially suitable when the effluents are treated in a collective centre. In the case of mobile ion exchangers, resins are restored in the collective centre. This procedure, which is particularly adapted to the case of small shops which do not produce effluents enough to justify individual waste water treatment facilities, should increase in proportion to the development of the collective treatment plants.

3.1.1.2. The concentrated effluents

The concentrated effluents should be treated in plant or in a collective treatment plant along the following lines :

. Cyanide or hexavalent chromium removal,
. Neutralization and precipitation of metal hydroxides
. Flocculation and clarification,
. Dewatering of sludges,
. Disposal of sludges.

3.1.2. Treatment processes

(Refer Annex C : Treatments of effluents)

3.1.2.1. Cyanide removal

Although the most commonly used reactives for cyanide removal, hypochlorites, allow for the oxidation of cyanides into CO_2 and N_2, the treatment of cyanides is at present limited to their oxidation into cyanates. This is definitely a case of a detoxification and not a destruction, for cyanates are discharged in their original state into the receptive medium. Furthermore, this oxidation is accompanied in most cases by a considerable production of salts which can be estimated at 30 kg of salts expressed in Na Cl per kg CN.

The catalytic combustion is suitable to oxidize cyanides into CO_2 + N_2, but investment costs make this process reserved to collective centres.

3.1.2.2. Hexavalent chromium removal

The hexavalent chromium cannot be settled as hydroxide, accordingly, it must be first reduced to trivalent chromium which is then treated as other metals. Reduction agents are bisulfite, sulphur dioxide or ferrous sulphate ; production of salts, expressed in Na SO_4 can be estimated at 10 kg per Kg CrVI.

3.1.2.3. Neutralization precipitation

The treatment of acids, bases, fluorine, and nitrites usually means the production and discharge of salts (Na Cl, Ca SO_4, Na NO_3, Na_2 SO_4...) only the phosphates being easily insolubilized.

The pH is then adjusted between 8 and 9 by the addition of sodium hydroxide (more expensive) or of lime (sludge volume more copious). The metals and fluorine are thus insolubilized by the precipitation of hydroxides up to the technical limits of the solubility product under the treatment conditions.

3.1.2.4. Flocculation - clarification

Clarification is the gravitational separation of suspended solids. Flocculants or polyelectrolytes may be added to make coagulation easier. The content in solids of the sludges issued from the clarifier varies from 0.5 to 3 %.

3.1.2.5. Dewatering of sludges

Any increase in solid contents of sludges involves a very important decrease in their volume : for example, 100 liters of sludge at 1 % of dry matter become after dewatering 4 liters of sludge at 25 % of dry matter. This dewatering is required especially as the areas agreed for the hydroxide sludge landfilling are usually few : accordingly,these sludges will sometimes be transported over quite a distance.

Dewatering of sludges is achevied by filtration usually up to 25 % of dry matter with a filter press or deep bed filter.

3.1.2.6. The disposal of sludges

Sludges are most often disposed to landfill. A process of chemical fixation of sludge is sometimes applied : a physical-chemical matrix structure ties up liquids and solids for disposal. This structure prevents, or at least retards leaching. But, in spite of their theoretical impact, the efficiency, to a commercial scale, of many processes already available commercially should be ensured before "fixed sludges" may be considered as inert wastes, and in particular, the long term efficiency of these structures shoud be ensured.

Encapasulation, i.e. packaging and containment of a specific quantity of sludge, high temperature heat treatment (1100 - 1200°C) of sludges and disposal to land of a slag are procedures which are rarely used, but capable of being developed.

3.1.3. Recovery

Metals from additives or from the substrate may be recovered and valuated from any stage of the effluent production or treatment. The additives in question are particularly the constituents of spent plating baths and sometimes those which cannot be recycled in their initial state into the technological chain.

Metals from the substrate can be recovered by a continuous electrolysis of the electroless plating bath (Refer to Annex A : the case of copper pickling).

The metal salts added to the plating baths may be recovered from spent baths by eletrolysis (copper) or, in some cases when the current efficiency is too low, by chemical removing and cristallysation of salts (nickel).

Recovery of diluated effluents may be achieved in the case of in-line treatment : the effluents are not mixed, so recovery is easier. Moreover, the techniques of effluent treatment may be designed to this end.

The electrolysis of the cake from hydroxide sludge filtration is sometimes achieved to recover metals, but it may only be practiced when the sludges contain only one metal which could be recovered in a pure form.

Metal from electrolytic recovery has a high purity and recristallysed salts have a sufficient purity for many uses, so these metals and metal salts are valued . But the major difficulty is more often the lack of marketing possibilities for these metals than to design techniques of recovery.

3.2. ECONOMIC IMPACT OF THE VARIOUS PARTS OF AN EFFLUENT TREATMENT STATION

TABLE 18 : ECONOMIC IMPACT OF THE VARIOUS PARTS OF EFFLUENT TREATMENT

	STATION	INVESTMENT (FF 1979)	CAPACITY	MAJOR FACTORS OF THE TOTAL COST
1	Storage areas	15,000 to 130,000 FF	0.5 to 30 m3	Surface of the shop Volume of the baths
2	System of pipes for collecting	30,000 to 150,000 FF		Plating variety Distance Storage selection
3	Dewatering	30,000 to 1,300,000 FF	2 to 50 m3/hr	Technique decisions Flows Facilities
4	Storage of concentrated effluents sludges and reagents	5,000 to 300,000 FF		Volume of spent baths and eluates Reagents supply Flux Facilities
5	Chromium removal	50,000 to 150,000 FF	0.5 to 5 m3/hr	Process Feasibility of installation Flows
6	Cyanide removal	50,000 to 150,000 FF	0.5 to 5 m3/hr	Process Feasibility of installation Flows
7	Neutralisation	40,000 to 150,000 FF	0.5 to 20 m3/hr	Process Feasibility of installation Flows
8	Flocculation Clarification	50,000 to 210,000 FF	0.5 to 20 m3/hr	Flows Facilities Flux
9	Final neutralisation	40,000 to 150,000 FF	0.5 to 20 m3/hr	Process Feasibility of installation Flows
10	SLudge dewatering	80,000 to 500,000 FF	0.5 to 50 T metal/year	Flows of metals Technique decision
	TOTAL	345,000 to 3,240,000 FF		

Total cost areas for each station may be very large (see graphic 19) because of variable factorspecular to each particular case.

Technical decisions and feasibility of installation of stations 3,4,8 and 10 which are the most expansive ones should be pointed out .

The experience shows that the annual operating costs of such facilities are usually between 10 and 20 % of the total amount of investment. Accordingly, savings on investment will be reflected in operation costs.

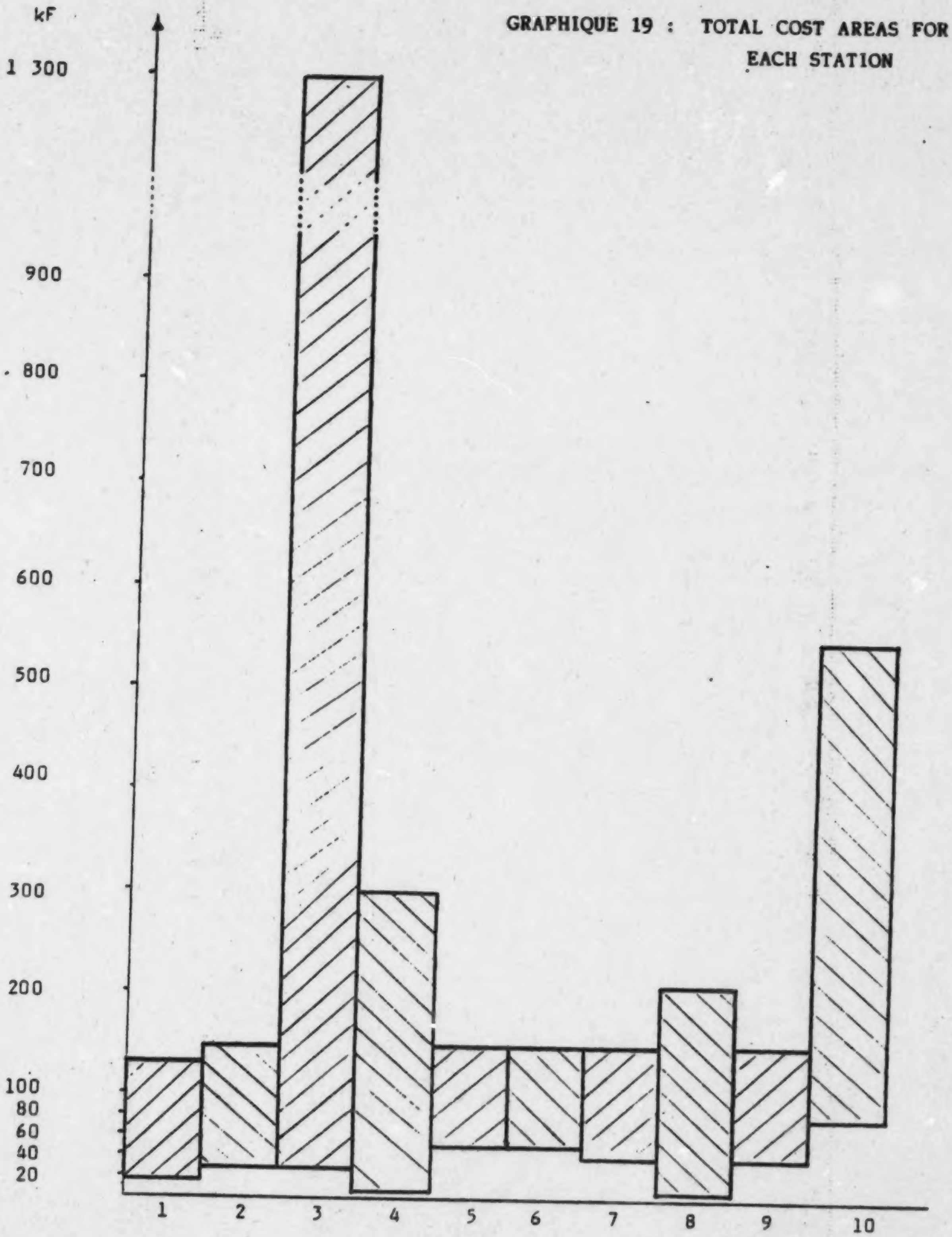
Calling in collective treatment plants involves a part of the investments required by stations 5,6,7,8 and 10 to be transfered on to stations 3 and 4 and an increase of a few points in the ratio of $\frac{\text{operation costs}}{\text{Investment}}$

Moreover, the eventuality of purification in a collective treatment plants favours individual treatment of the type :

Multiple rinses + dewatering

Global estimations for stations 3 and 4 are not sensitively modified, but in this case facilities have only five stations :1, 2, 3, 4 and 9.

GRAPHIQUE 19 : TOTAL COST AREAS FOR EACH STATION



- 4 -

LEGISLATION AND PRACTICE OF EFFLUENT TREATMENT IN THE VARIOUS COUNTRIES

4.1. LEGISLATION AND RULES

4.1.1. Federal Republic of Germany

General legislation might apply to metal finishing shops with regard to licensing of facilities, safety conditions, etc... Moreover, metal finishing shops in the Federal Republic of Germany are subject to hazardous waste and waste water legislation.

1. Solid Waste legislation :

   Metal finishing wastes or sludges are subject to the general provision of the Waste Disposal Act. They may be treated and disposed of in licenced facilities only. For collection and transport of these wastes a collection permit is necessary.
   Most of these wastes are regarded as special wastes or hazardous ones. For these wastes, the tripticket procedure applies automatically, they are regarded as notifiable wastes, i.e. the owner of these wastes has to give notice of his ownership to the competent authority. Waste producing facilities have to appoint a "Factory Inspector for Wastes" according to the "Regulation on Factory Inspector for Waste" made under the Waste Disposal Act.

2. Waste Water legislation :

   The general principals for waste water legislation are summarized in "Regulation and Legislation Control of the Discharge of Pollutants into Surface Waters".
   In pursuance of § 7a of the Federal Water Act, a working group is established to make recommendations on the work on the generally accepted state of the art for the quality of metal finishing effluents. The Federal Government will issue an administrative decree giving minimum requirements for the discharge of these waste waters into surface waters, which will be binding for all licensing authorities in Germany.
   For discharges using a sewer and passing public waste water treatment plants, local regulations apply, issued either by the authority responsible for waste water disposalor by the enterprise taking care for it.

3. Public aid :

   Aid by the public administration is being applied in the following ways :
   Financial assistance by means of depreciation of capital investment for goods that serve environmental protection according to § 7d of the Income Tax Law. This incentive makes it possible, upon application, to write off 60 % of the investment in the first year. This financing assistance, however, is limited to enterprises and plants erected before Jan. 1, 1975. Upon objection of the E.E.C. this sort of financing assistance is only conceded till 1981.
   Financial aid in the construction of public, control treatment and disposal facilities.

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4.1.2. France

For several years, some juridical, administrative and financial provisions force metal finishing manufacturers to manage more strictly their wastes and, im most cases, to modify their operation processes.

1. The legislation relating to "Scheduled facilities" has been the subject of particular technical guidelines as far as metal finishing is concerned. Especially, according to the nature of the receptive medium, effluents are required to be treated more or less severely (A or B treatment) to comply with the following characteristics :

	A	B
	pH 5 to 9	pH 5 to 9
Cyanides oxidable by chlorine (mg/l)	0.1	1
Hexavalent chromium (mg/l)	0.1	0.1
Cadmium (mg/l)	3	3
Sum of metals (mg/l) (Zn + Cd + Cu + Fe + Ni + Cr)	15	15
Fluorides (mg/l)	15	

Old shops had to be in accordance with the guidelines relating to new shops by the 1st of September 1980. Investigations should allow this to be taken into account.

2. The "Waste Disposal and Material Recovery Act" of the 15th of July 1975 makes manufacturers responsible for their wastes until they are disposed of in satisfactory conditions.

3. Relating to the fight against water pollution, a financial inciting system was provided applying the "polluter-payer" principle. Metal finishing manufacturers must pay fees to the "Basin Financial Agencies" by reason of inhibiting material discharge into waters. These fees are calculated with respect to the quantity and the toxicity of the consumed substances. They are used to finance the performance of public interest works either in managing water resource, or in fighting against pollution. The agencies supply these operations with their technical and financial means.

4.1.3. United States

Applying subtitle C of the "Resource Conservation and Recovery Act" of 1976, the EPA is entitled to prepare rules allowing for the monitoring of any significant quantity of hazardous waste from its generation to its final disposal. These regulations schemes were published in the Federal Register.

Seven sections of Subtitle C deal with hazardous waste management :

- "Definition, identification and listing of hazardous waste" (section 3001)
- "Standards applicable to generators of hazardous waste"(section 3002)
- "Standards applicable to transporters of hazardous waste" (section 3003)
- " Performance, design and operating requirements for facilities that treat, store or dispose of hazardous waste" (section 3004)
- "A permit system for such facilities (section 3005)
- "Guidelines to assist states in developing their own hazardous waste programs and procedures for obtaining EPA authorization for their programs" (section 3006)
- "Procedures by which hazardous waste generators, transporters and facility owners/operators notify EPA of their activities (section 3010).

Furthermore the EPA has published rules under the Clean Water Act which control direct discharges of metal finishing wastewaters to navigable waters (effluent discharge limits), and which prescribe pretreatment of metal finishing wastewaters prior to discharge to sewers leading to publicly owned treatment works.

4.1.4 Canada

The Federal Government in Canada has issued " Metal Finishing Liquid Effluent Guidelines" under the authority of the Fisheries Act which prohibits the discharge of deleterious substances to water frequented by fish. In addition, some of the provinces have their own regulations under the authority of provincial legislations. The federal guideliness are based on "best practicable technology" and serve as the national baseline requirements. The province may, however, implement more stringent requirements on the basis of local needs. The management of sludges and solid wastes fall within the juridiction of the provinces.

4.1.5. Netherlands

Article 31 of the Chemical Waste Act says it is prohibited to dispose of chemical waste (including hydroxyde sludges) on or in the soil, wether via container or otherwise. Exemption can be granted, but only in exceptional circumstances.

The Chemical Waste Act is based on a licence system for storing, treating, processing and destroying of chemical wastes.

The generator of chemical waste is free to dispose of these substances under his own control in accordance however, with the other legislation on the subject (e.g. Air Pollution Act, the Pollution of Surface Waters Act, Public Nuisance Act).

4.1.6. United Kingdom

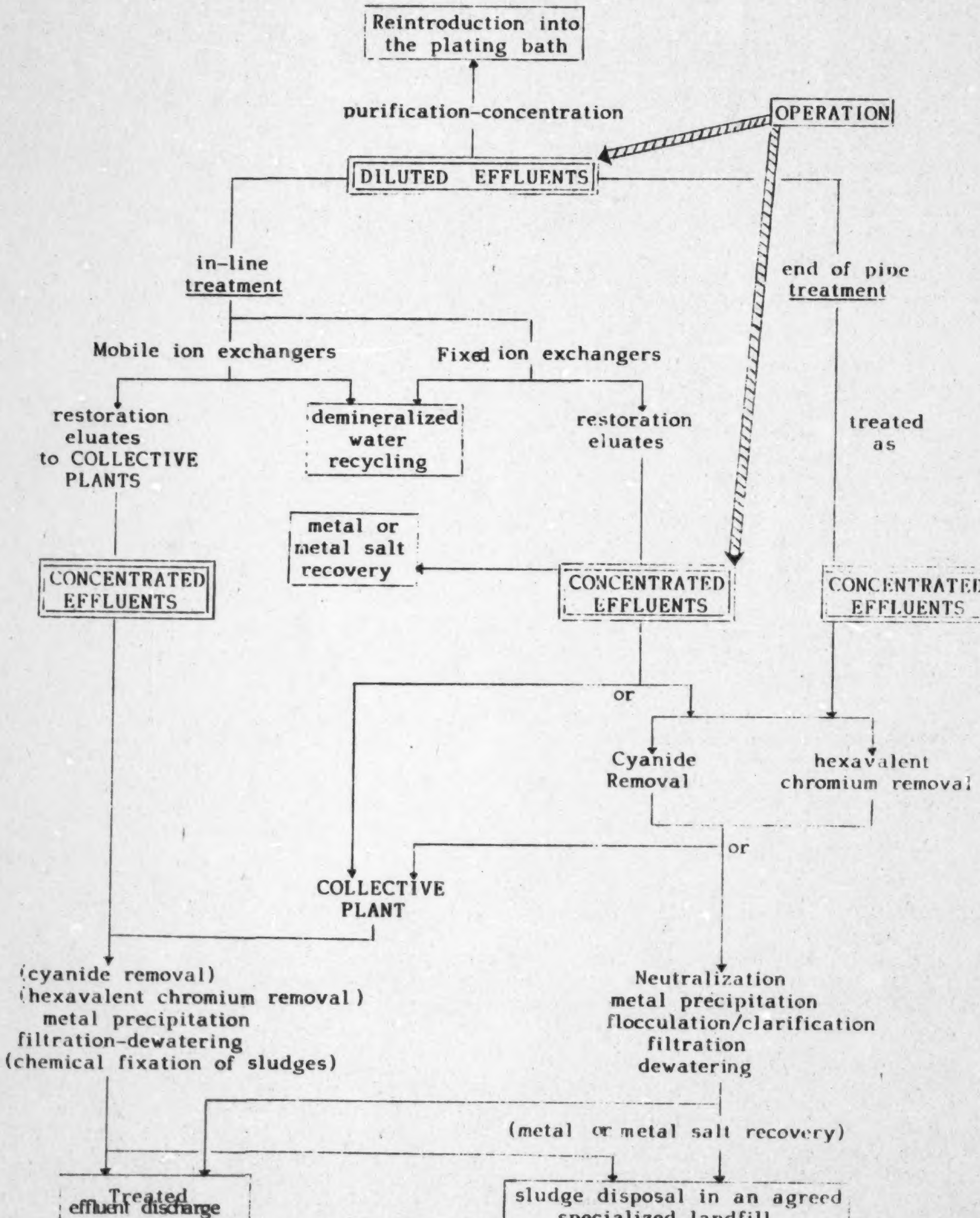
In the department of the Environment's Waste Management Paper (WMP) series a Technical Memorandum on Metal Finishing Wastes has been produced (WMP11). This includes guidelines in the form of a Code of Practice on the treatment and disposal of these wastes.

Under Part I of the Control of Pollution Act 1974, the landfill disposal of metal finishing wastes can only take place on appropriately licensed sites. Likewise, the external treatment of such wastes can only be carried out at a licensed facility.

Under Part II of the ACT all earlier water pollution legislation has been consolidated, but not yet brought into force, so that under existing legislation the discharge of metal finishing effluents to surface waters or, more commonly, to sewers must only take place under Consent conditions issued by the water authority. Pretreatment is likely to be necessary to meet the conditions imposed.

4.2. TREATMENT

DIAGRAM 20 : EFFLUENT TREATMENT LINES IN FRANCE


Reintroduction into the plating bath
purification-concentration
OPERATION
DILUTED EFFLUENTS
in-line treatment
end of pipe treatment
Mobile ion exchangers
Fixed ion exchangers
restoration eluates to COLLECTIVE PLANTS
demineralized water recycling
restoration eluates
treated as
metal or metal salt recovery
CONCENTRATED EFFLUENTS
CONCENTRATED EFFLUENTS
CONCENTRATED EFFLUENTS
or
Cyanide Removal
hexavalent chromium removal
or
COLLECTIVE PLANT
(cyanide removal)
(hexavalent chromium removal)
metal precipitation
filtration-dewatering
(chemical fixation of sludges)
Neutralization
metal precipitation
flocculation/clarification
filtration
dewatering
(metal or metal salt recovery)
Treated effluent discharge
sludge disposal in an agreed specialized landfill

4.2.1. Federal Republic of Germany

Less than 5 % of waste waters are discharged directly in the natural medium. 95 % of waste waters (i.e. 150 x 10^6 m3 in 1976) are discharged to sewerage systems after pretreatment :

. 50 % of waste waters are de-cyanided. The relating investment is about 20,000 DM for a flow of 10 m3/hr.

. 60 % of waste waters are de-chromated. The relating investment is about 20,000 DM for a flow of 10 m3/hr.

. 100 % of waste waters are neutralized. The relating investment is about 100,000 DM for a flow of 10 m3/hr.

Operating costs of a pretreatment station are included between 60 and 150 DM/m3.

From very small shops often no effluent treatment is demanded. In the area of the Ruhrverband, for instance, c.a. 100 enterprises out of 784 metal processing firms have no effluent treatment. Such enterprises generally have to submit their spent baths and rinsings to a central detoxification plant. However 90 % of the spent baths are treated by conventional chemical processes :

- cyanides are removed by hypochlorites in central plants and in 90 % of the cases of individual treatment ; other processes are used for high concentrations, especially catalytic oxidation (8 %) ;
- hexavalent chromium is commonly removed by bisulfite, sometimes by sulphur dioxide ;
- required investments for cyanide and hexavalent chromium removal-neutralization facilities are about 150,000 to 200,000 DM for a flow of 10 m3/hr. Operation costs are included between 100 and 300 DM/m3.

This individual detoxification procedure promotes a specific treatment for variously constituted effluents.

Moreover, up to 10 % of all electroplating enterprises employ ion exchangers for up concentrating the metal contents in their rinsings, the eluates then likewise being treated chemically.

A mobile treatment unit is studied. Transfer facilities are provided, some of which will be managed for neutralization and sludge dewatering.

88 % of hydroxide sludges generated by the effluents treatment (i.e. 440,000 T/year) are disposed in landfill including 20 % codisposed with domestic wastes and 80 % on areas reserved to hazardous wastes. Their water content commonly varies from 60 to 70 %.

4.2.2. Netherlands

As to the larger quantity, the rinsing water-stream will always be handled intern, first with simple methods to purificate the rinsing water and later on, if necessary, with a detoxification-neutralization-dewatering installation.

There is no specialized centre operating with the concentrated effluents treatment in the Netherlands, but some private enterprises are active in this field. Two companies run a commercial detoxification-neutralization-dewatering installation and one firm utilizes the surplus capacity of its own installatin to treat concentrates for others. The market situation is still quite obscure and treatment costs are sometimes high.

About 20 Detoxification-Neutralization-Dewatering installations for rinsing waters are operational at the moment in the Netherlands. The detoxification step, if necessary, for CrVI is mostly carried out with sulphites (80 %) or with ferrous iron (20 %), for cyanides, this is generally done with hypochorites. The neutralization is mostly carried out with NaOH (80 %), in some cases (20 %) this is done with a $Ca (OH)_2$ solution. The dewatering process is done with a standard filterpress.

2 000 T/year of hydroxide sludges, with an average water content of 70 % are yet disposed in landfill in spite of a new reglementation (see 4.1.5.) for a cost varying from 100 and 300 Fl.
500 T/year are heat-treated for a cost of 250 Fl.

4.2.3. U.S.A.

About 80 % of electroplating shops discharge their effluents to public sewage systems. Waste water treatment plants thus receive 4 million m3/day whereas 80 million m3/day are discharged to receiving streams.

Most manufacturing process solid wastes are disposed in municipal landfills.

The best current treatment/disposal practice for water pollution control sludges is :

- Solids concentration,
- Dewatering to a greater than 20 % solids "cake",
- Disposal in a sanitary landfill approved by a State Authority for receiving wastes of this nature.

In fact, the prevalent treatment and/or disposal practice for water pollution control sludge is concentration to 1.5 % solids contents, followed by land disposal.

Degreaser solvent sludges and electroless nickel plating wastes are typically disposed in landfills.

Since many metal finishing sludges are defined as hazardous waste in new EPA regulations, current treatment and disposal practices for the sludges will have to change. Under new rules which become effective in November 1980, all hazardous wastes must be treated, stored or disposed of only in licensed hazardous waste facilities.

4.2.4. United Kingdom

The most usual method of effluent disposal in the UK is to discharge the effluents, after suitable pre-treatment, to a public sewerage system .Control over the quantity and quality of such discharges is exercised by regional water authorities, who are empowered to impose appropriate conditions before consent is granted to make the discharge.

Where treatment is required before the effluent is descharged, it is usually given on the premises of the effluent producer rather than in specialist treatment centres, although small volume arisings of liquid wastes such as spent process solutions and reagents are in some cases sent to treatment centres for detoxification or recovery. In addition, at least one organisation in the UK is looking into the possibility of providing a mobile effluent treatment service to meet the special needs of small finishing companies where the provision of on-site treatment facilities is made difficult and expensive by the relatively small volumes of effluent produced.

At present, about 100,000 tonnes per annum of sludges from effluent treatment are produced in the UK, and most of this quantity is disposed to landfill sites. These wastes are predominantly in the form of thickened or unthickened slurries (solids content up to 5 % by weight), though arisings from larger premises are often in the form of partially dewatered sludges(solids content up to 30 % by weight). The number of landfill sites which currently accept such wastes is small, and in some cases, wastes are transported for distances up to 300 km before disposal.

The quantities of sludge at present sent for recovery processing are small (probably less than 4,000 tonnes per annum for the entire industry), though this quantity could be increased depending on economic factors and the availability fo single-constituent dewatered sludge rather than mixed hydroxides. The only metallic-bearing sludges currently being processed for recovery on a large scale are nickel carbonate, which is principally produced by the larger electroplating installations, and copper hydroxide. Copper is also recovered by cementation from certain applications.

Disposal to sea of metal-containing sludges is limited by international agreements and by national requirements, the operation in the UK being controlled by licences issued by MAFF/DAFS. Although this disposal route is seen as part of the overall waste disposal strategy, it is used only to a limited extent and in appropriate cases.

4.2.5. France

In spite of new juridical provisions, it is yet difficult to grasp detoxification and disposal circuits of metal finishing waste because of the multiplicity of situations.

Shops disposing of required facilities for the effluent treatment or even shops turning to collective treatment plants are few.

For example :

. 53 % of metal finishing shops in the Rhône Mediterranée Basin do not achieve any treatment prior to the effluent discharge,

. In 1976, investigations from local authorities allowed for registration of shops whose discharges are in agreement with the 1972 guidelines.

BATH CAPACITY	% OF SHOPS IN IN THE SAMPLE	RATE OF AGREEMENT WITH 6.6.1972 GUIDELINES
less than 5,000 l	39 %	25 %
5,000 to 20,000 l	36 %	33 %
More than 20,000 L	25 %	38 %

The major objective is the conformity of shops working with a bath capacity more than 20,000 l.

. Efficiency rate of effluent treatments (schematic results from application of contractual factors used by the Basin Agencies)

ADOUR GARONNE	ARTOIS PICARDIE	LOIRE BRETAGNE	RHIN MEUSE	RHONE MEDITER.	SEINE NORMANDIE
50 %	65 %	35 %	25 %	50 %	40 %

1. Individual treatment

Diagram 20 shows the major circuits of metal finishing effluents purification.

Diluted effluents may be submitted to in-line treatment or to end-of-pipe treatment. In the case of an in-line treatment, ion exchangers allow for effluent concentration, and production of pure water often demineralized which may be recycled. Therefore, such a treatment is commonly chosen for most diluted effluents which are then treated with concentrates. The diagram shows that turning to collective treatment plants may happen at various stages of the detoxification process. For example, it seems that a number of shops owning cyanide or hexavalent chromium removal facilities, have no facilities for dealing with metal insolubilization.

The difficulties in operating end-of-pipe treatments, especially in the case of concentrated effluents, may lead manufacturers to turn to collective treatment plants for the detoxification of their concentrated effluents.

2. Collective treatment plants

Four collective treatment plants deal with the physico-chemical treatment of great amounts of toxic wastes, three only with cyanide removal :

– Hexavalent chromium is reduced by sulphur dioxide or ferrous sulphate. The treatment cost by sulphur dioxide is lower, this is an explanation of the various invoiced prices, for example :

. 350 to 400 FF/T for contents lower than 5 g/l
. 400 to 500 FF/T for contents around 50 g/l
. 450 to 700 FF/T for contents around 100 g/l.

- Cyanides are removed by catalytic oxidation of hydrocianic acid stripped with sulphuric acid, finishing with hypochlorites then with persulphuric acid and precipitation-filtration.

Prices invoiced by collective treatment plants are :

- 400 to 500 FF/T for contents lower than 5 g/l
- 600 to 600 FF/T for contents around 50 g/l
- 750 to 800 FF/T for contents around 100 g/l.

(Collective treatment plants deal with cyanided hardening salts too : they are not treated by Cyan-Cat process, but by hydrolysis of cyanates from cyanide oxidation by hypochlorites),

- Subsequently to cyanide and hexavalent chromium removal, these effluents are mixed with other acid and alkaline effluents and neutralized. Medtal hydroxides are precipitated, most often by lime, and sludges are involved.

These sludges are dewatered. Most collective treatment plants employ chemical fixation processes prior to sludge disposal on impervious aeras.

4.3. CONTROL - RECOVERY

This item deals with global pollutants control rather than with loss control.

It is not possible to give a numbered account of the control techniques used in the various countries. However, the Federal Republic of Germany made several observations of general interest.

Reasons why the low-waste electroplating shop does not yet exist everywhere

On the whole, this branch of industry has an unfavourable structure which restricts the use of modern tehnologies. For most small to medium sized shops the installation and maintenance of new systems leads to unjustifiable costs, because reusable substances can only be recovered profitably with large quantities of residues of uniform composition. Quite apart from this, many shops simply do not have the space for additional equipment, because the building itself or the structural "entwinement" does not permit this.

In many cases, it is possible for small firms to burden the "wastewater network" at excessively low cost. Firms having wastewater purification plants commonly operate on the once-through principle without the recovery of reusable substances. The inadequate maintenance and monitoring of, in part, outdated plants leads to the legally stipulated limits being exceeded. This "lax" operation of wastewater purification plants is comparatively low-cost and does not encourage measures aimed at making savings in raw materials.

The disposal network for hydroxide sludges is still relatively dense. Compacted, neutralized and decontaminated sludges are still today in some cases disposed of at low cost on company landfills or also on large orderly domestic refuse landfills. Hydroxide sludges which have not been dewatered and have not been completely decontaminated or neutralized can, often, be delivered to a collective treatment plant or to one of its collection points. Even this price still appears so reasonable to many operators that they give no thought to purchasing a filter press of their own or to optimizing their own decontamination plant. The situation is aggravated by the fact that connection to and use of the network is compulsory.

The enlightenment and information process was relatively late in starting in this branch of industry. Although every penny was counted at the incoming raw materials end and much money was also ploughed into automation in order to save labour costs, the economic nonsense at the waste end was seen too late in many cases. Small and medium sized firms have only recently become aware of the savings which are to be made in energy and raw materials.

Reasons why there will be more low-waste electroplating shops in future

It can be assumed, that, in the medium term, there will be far more low-waste electroplating shops. The term "low-waste electroplating shop" is also taken to include those firms which pass on their residues for external reprocessing in the sense of recycling. For many small-scale shops this will probably be the only workable solution anyway unless the number of "environmentally minded" electroplating shops is to increase in purely arithmetical terms as a result of the closure of many small-scale shops in the medium term.

There are also a number of reasons for the above thesis :

- the legislative provision, now achieved in the various countries and the enactments in preparation are generally very constraining for metal finishing manufacturers ;

- an overproportional rise in costs is taking place on all fronts and affects (in variable proportion from a country to another) :
  - raw material, energy and water costs,
  - personnel costs in shops with a low degree of automation,
  - costs of chemicals for decontamination and the operation of wastewater treatment plants,
  - collection and transport costs and the costs of treatment or disposal in a waste disposal plant.

- competition between the electroplating industry and its "rival", the painting industry, has become tougher. In partly overlapping markets it is necessary on the one hand to continue to pay great attention to quality, while, on the other hand, improving the image of electroplating and putting it on a par with that of the now 'environmentally minded" painting industry without all this resulting in random rises in the price of the end product.

These reasons, and perhaps others, have already promoted a special effort in most countries, to use some plating discharges in the chemical industry.

In the Netherlands for example, substance recovery is commonly subcontracted to collective treatment plants. Electrolytic recovered copper and zinc or thermal processing recovered zinc are usually traded.

In the Federal Republic of Germany, new treatment processes like the different membrane processes for metal reclamation are apparently hardly introduced ; they find application principally in the noble metal coating industry. Further progresses in the field of effluent treatment is promised by the development of recycling facilities that should reclaim losses of electrolytes in their original conditions.

Table 21 Recovery processes and their possible applications *

Type of process Main groups	Chemical processes		Physical processes			Electrochemical processes	
Sub groups	Precipitation	Ion-exchange	Reversed osmosis	Ultra-filtration	Evaporation Vaporization	Electrolysis	Electrodialysis
Possible applications	Precipitation of metals as metal hydroxide, metal sulphite, metal carbonate; direct decontamination	Nonferrous and noble metals from wastewater: purification of process solutions: chromic acid, chromatization, phosphoric acid	Separation of valuable substances from rinsing water, e.g. nickel, silver, copper, complexing agents etc	Separation of macro-molecular substances from waste-waters and process solutions, e.g. oil emulsion, alkaline wash solutions, degreasing baths	Concentration of heavily charged waste-waters from multiple cascades after chromium, nickel, copper, tin, cadmium and zinc baths	Separation of nonferrous and noble metals from wastewater and concentrates	Separation of ionogenically dissolved substances from waste-water and semi-concentrates
State of recovered product	Sludge	Aqueous solution	Aqueous solution	Aqueous solution	Aqueous solution	Solid	Aqueous solution
Chemical change in original material	yes	yes	no	no	no	yes	no
Possibility of direct recycling	no	in some cases	yes	yes	yes	yes	yes

* Table adapted from K.Beyer, Müll and Abfallhandbuch, (waste and refuse hand book), Erich Schmidt Verlag.

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COMMITTEE ON THE CHALLENGES OF MODERN SOCIETY
NORTH ATLANTIC TREATY ORGANIZATION

PILOT STUDY ON THE DISPOSAL OF HAZARDOUS WASTES

METAL FINISHING WASTES

°°°

ANNEXES

Final report prepared by FRANCE

100 % RECYCLED PAPER

CORRECTIONS TO THE ANNEXES

* "Work pieces" should be read instead of "slugs"

* "Sequences of plating operations" (for the deposit of a metal upon a substrate surface) should be read instead of "technological chains".

ANNEXES

ANNEX A : THE TECHNOLOGICAL CHAINS

The most polluting technological chains for metal finishing are presented :

A.1 Cyanided copper plating
A.2 Acid copper plating
A.3 Watts nickel plating
A.4 Decorative chromium plating
A.5 Thick chromium plating
A.6 Cyanided zinc plating
A.7 Acid zinc plating
A.8 Cyanided cadmium plating
A.9 Chromic pickling
A.10 Copper pickling
A.11 Steel pickling

The following are studied for each chain :

- specific field of use
- the bath characteristics
- location of the bath in the chain
- simplified substance balance
- control techniques
- case study
- technical variants

Low or non-polluting deposit processes are studied in A.12

A.12.1 Precoated metal
A.12.2 Vacuum metallization

ANNEX B : CONTROL TECHNIQUES

B.1 Straining
B.2 Static recovery rinse
B.3 ECO rinse
B.4 Ion Exchange
B.5 Evaporation
B.6 Reverse osmosis
B.7 Electrolysis
B.8 Electrodialysis

For each technique, the followings are presented :

- principle
- evaluation of reducing the pollution flux
- technical impact.

APPENDIX

B.A.1. Cost prices of control techniques
B.A.2. Calculation of rinses
B.A.3. Comparison of the ion exchanger recycling process and the multiple cascade rinse technique
B.A.4. New techniques and new applications of control techniques
B.A.5. Recommandations for the insertion of controle techniques in a workshop

ANNEX C : EFFLUENT TREATMENTS

Characteristics and application area of each technique :

C.1. Integrated treatment
C.2. Cyanide removal
C.3. Chromium removal
C.4 Final neutralization and precipitation of metals
C.5. Effluents clarification
C.6. Dewatering of sludges

APPENDIX

1 : New effluent treatment techniques
2 : Cost prices of effluent treatment techniques

ANNEX A

TECHNOLOGICAL CHAINS

A.1. CYANIDED COPPER PLATING

. Electrolytic treatment

. Hot bath

A.1.1. Utilization

The electrolytic deposit of copper in a cyanided medium is mainly used as a nickel or chromium nickel deposit undercoating upon substrates like :

- Zamac
- Copper metals (brass, nickel, silver, etc...)
- Steel.

It is indispensable to ensure the adhesion of electrolytic deposits upon zamac, which is still frequently used on copper metals even though it tends to disappear in many applications as an undercoat over steel.

It also serves as an underlying layer of another copper deposit (in acid medium) used for its brightening and levelling properties which is impossible to deposit directly upon steel and zamac.

The deposit is applied :

- either in the frame,

- or in the drum.

A.1.2. Characteristics of a cyanided copper plating bath

Standard composition :

. CNCu	25 g/l
. CNNa	35 g/l
. Sodium carbonate	30 g/l
. Rochelle salt	45 g/l
. Soda for pH	12-12.5
. Brightener	according to supplier
. Penetrant	

Sodium is sometimes substituted by potassium :

. Metal Cu	20 g/l
. Free KCN	25 g/l
. KOH	15 g/l
. Rochelle salt	50 g/l
. K_2CO_3	

Temperature : 45 to 60° C.

Density of current : 1 to 5 A/dm^2

Current yield : 60 to 70 %

Speed of deposit : 50 microns at 3 A/dm^2

Anodes : pure copper, metallurgical or electrolytic, bagged.

Anode/cathode ratio : 2/1

Ampere/liter ratio : less than 1

Agitation and filtration : required

The metallic copper is found in the bath in the form of a cyanided complex which serves as a vehicle between the anode and the cathode.

$$Na\left[Cu\ (CN)_2\right] \text{ and } Na_2\left[Cu\ (CN)_3\right]$$

Dissociation of the complex takes place in two phases by passage of the current :

- $Na\left[Cu\ (CN)_2\right] \leftrightarrows Na + Cu\ (CN)^-_2$ well dissociated
- $Cu\ (CN)^-_2 \leftrightarrows Cu^+ + 2\ CN^-$ very little dissociated

"Free" cyanide is indispensable for a proper anode corrosion - anode dissolution increases with the concentration of free cyanides.

Rochelle salt also serves to corrode the anodes.

Soda and sodium carbonate serve to maintain the pH.

A.1.3. Location of the bath in the chain

Over brass steel	Over Zamac	Over Zamac in the drum
- chemical degreasing	- chemical degreasing	- Chemical degreasing
- Rinsing	- Degreasing	- Rinsing
- Electrolytic degreasing	- Ultra-sound	-CYANIDED COPPER PLATING
- Rinsing	- Electrolytic degreasing	- Rinsing
- Acid depassivation	- Rinsing	- Nickel plating
- Rinsing	- Acid depassivation	- Rinsing
-CYANIDED COPPER PLATING	- Rinsing	
- Rinsing	-CYANIDED COPPER PLATING	
- Acid rinsing	- Rinsing	
- Acid coppering	- Nickel plating	
- Rinsing	- Rinsing	
- Acid depassivation	- Chrome plating	
- Rinsing	- Rinsing	
- Nickel plating		
- Rinsing		
- Chrome plating		
- Rinsing		

The term "rinsing" designates the "rinsing function" and implies several tanks.

A.1.4. Simplified substance balance

The wastes generated during the operation of such a bath are the following :

Wastes by drag out :

Drag out in the rinsings of a volume of solution having the exact characteristics of the deposit bath ;

Wastes from maintenance :

They include :

- liquid losses by restoring the filters of the continuous filtration,
- liquid losses during the manipulation of the bath to do curative or preventive treatments to eliminate impurities (i.e. activated carbon)

Wastes in steam :

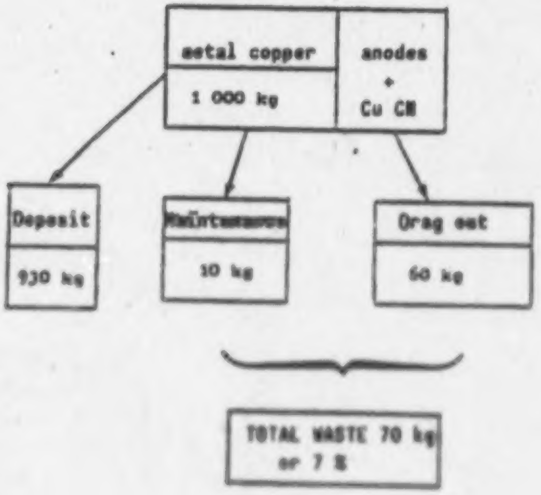
Because of the application temperature and anodic and cathodic efficiency < 1, with result in a vesicular emission in steam.

These are mainly cyanide wastes.

Wastes by degradation :

The anodic phenomena, the temperature, the boiling of the bath, generate a degradation of the sodium carbonate ion CN^-, the high concentrations of which may be detrimental to the functioning of the bath.

COPPER PLATING-FRAME


metal copper
1 000 kg
anodes
+
Cu CN
Deposit
930 kg
Maintenance
10 kg
Drag out
60 kg
TOTAL WASTE 70 kg
or 7 %

The greatest losses are :

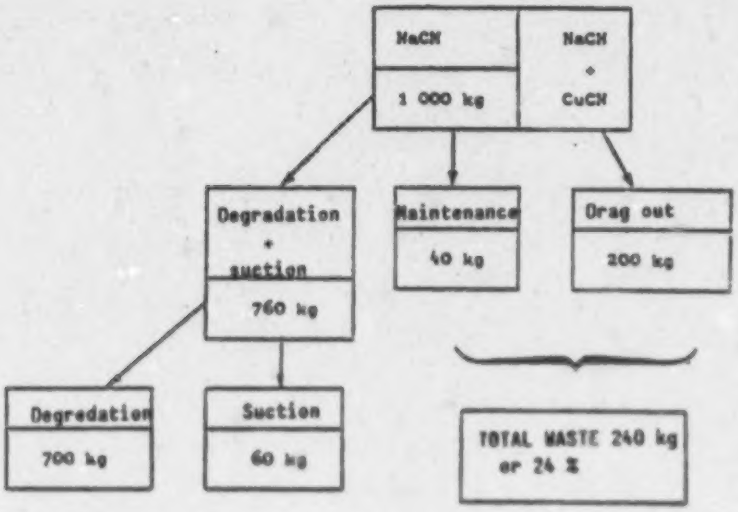
- drag out
- degradation

Product consumption of this kind of bath by order of quantity shall be :

1) Na CN + copper anodes

2) Other bath components + additives.

COPPER PLATING FRAME


NaCN
1 000 kg
NaCN
+
CuCN
Degradation
+
suction
760 kg
Maintenance
40 kg
Drag out
200 kg
Degradation
700 kg
Suction
60 kg
TOTAL WASTE 240 kg
or 24 %

A.1.5. Control techniques

Straining +

Static recovery rinses +

Decrease rate in copper losses by drag out : 98 %

Cascade static rinses balance hot copper plating bath losses in suctions.

Metallic copper may be recovered by electrodialysis of rinsing waters. Cyanides are somewhat oxidized. Copper may be valorized in the form of anode in the plating bath.

A.1.6. Case study

Copper plating in the drum upon Zamac :

Bath : 5.75 m^3, 43 g Cu/l

Drag out : 1.07 l/drum (0.071 l/kg)

Straining : 20 sec. (plating bath) and 10 sec. (rinsing)

Copper losses : 22.7 % : 22.52 % rinsing
0.18 % miscellaneous

Provision :

Cyanided copper plating ←
Static rinse
Static rinse
Static rinse
Running rinse

The solution of three cascade static rinses allows for balancing hot copper plating bath losses by suction.

Copper losses : 0.27 % : 0.05 % rinse
0.24 % miscellaneous.

Decrease in the copper pollutant flow : 99.08 %
in rinses : 99.9 %

A.1.7. Technical variants

Removal of cyanided copper plating on brass or steel substrate :

Improving the surface preparation series and nickel plating -chromium plating operation. Nickel may be deposited directly upon the substrate.

The quality of the coating produced by the Ni-Ni-Cr chain is at least equal to the one from the Cu-Ni-Cr chain and is superior when considering its anti-corrosion properties on steel substrate.

The trend is for the general application of this process on steels for which the potential substitution rate is about 95 %. The substitution rate is about 50 % for copper because of the diversity of the alloys to be treated. This serie is particularly applicable to bass. It is impossible to apply the Ni-Ni-Cr treatment to Zamacs because of the technical necessity of an underlying layer of copper.

Using the Ni-Ni-Cr series allows for the economy of four rinse baths and one cleaning bath, and the economy of a special canide storage, as the effluents from the first nickel treatment are compatble with the total effluents of the chain.

As the cyanided copper plating and nickel plating bths are hot baths, substitution does not cause any noticeable modificaton. In both cases, static rinsing permits the treatment baths to be balnced and as a result 95 % of the drag out to be recycled.

The storage of effluents from the maintenance of circuits for cyanided products is no longer necessary.

Utilisation of alkaline copper plating bath based pyrophosphate (without canides)

Alkaline copper plating with copper pyrophosphate (20 g/l) and potassium pyrophosphate (L.50 g/l)at 50-60 ° with pH between and 9.2, may substitute the cyanided copper plating baths, but this proces is used very little because of a more important maintenance than for the cyanided bath, and with less performing results.

Copper fluoroborate baths

Substituting fluoroborates for cyanides decreases environmental pollution, as the fluoroborates are substantially less toxic than the cyanides.

For technical reasons, fluoroborates are practically used for thick deposits and mainly for Sn-Pb deposits in the manufacturing of printed circuits.

Furthermore, the chemical agents used are expensive and none of the processes of fluoroborate recovery in the rinse waters has been perfected yet. A process using electrodialysis and ion flotation is under study.

As the cyanided copper plating occurs in a hot bath, the decrease in volume of the bath may be compensated by adding two static rinse baths, which prevents cyanides from being discharged.

A.2. ACID COPPER PLATING - SULPHATE BASE

- Electrolytic treatment
- Cold bath

A.2.1. Utilization

The copper electrolytic deposit in a sulphate based acid medium is mainly used in decoration and anti-corrosion as an undercoat which adds gloss and levelling to the nickel-chromium deposits on the metal or plastic substrates (ABS).

It is deposited upon an alkaline copper layer over substrates like zamac and steel or upon a nickel coating over a steel substrate.

The direct deposits of acid copper upon cuprous matter are possible, but not widely used.

A.2.2. General characteristics of a glossy acid copper plating bath

Composition :

- Hydrated copper sulphate : 200 to 250 g/l
- Sulphuric acid : 50 to 70 g/l
- Sodium chloride : 50 to 100 mg/l
- Additional agent : depending on supplier

Temperature : optimum 25° C
Current density : 3 to 6 A/dm^2
Current efficiency : 95 %
Deposit velocity : 60 microns/h at 5 A/dm^2
Nature anodes : phosphorus copper, bagged
Anode/cathode ratio : 2/1
Ampere/liter ratio : 1/1
Agitation : blowed air
Filtration : continuous

A.2.3. Location of the bath in the chain

upon steel-brass-zamac	upon steel
Ultra-sonic degreasing	Electrolytic degreasing
	Rinsing
Rinsing	Electrolytic degreasing
Electrolytic degreasing	Rinsing
Acid depassivation	Pickling
Rinsing	Rinsing
Cyanided coppering	Nickel plating
Rinsing	Rinsing
Acid depassivation	Acid depassivation
Rinsing	Rinsing
ACID COPPERING	ACID COPPERING
Rinsing	Rinsing
Nickel plating	Nickel plating
Rinsing	Rinsing
Chromium plating	Chromium plating
Rinsing	Rinsing

The term "rinsing" designates the "rinsing function" and implies several tanks.

A.2.4. Simplified substance balance

The wastes generated during the operation of such a bath are the following :

Wastes by drag out :

Drag out in the rinsings of a solution volume having the same characteristics as the plating bath.

Maintenance wastes :

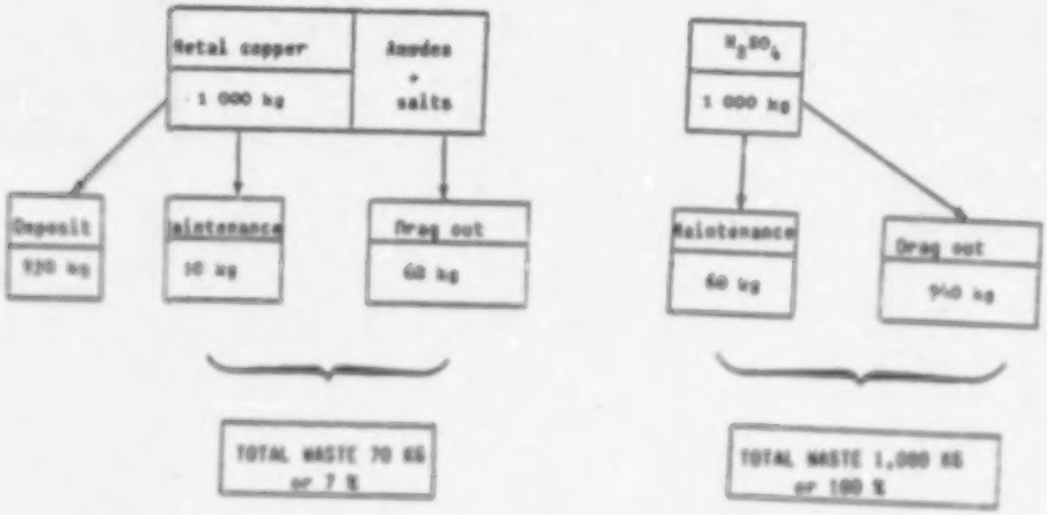
They include :

- liquid wastes generated by replacing the filters of the continous filtration,
- liquid wastes generated during manipulation of the bath to do curative or preventive treatments.

Wastes by drag out represent the largest amount of wastes.

Product consumption of such a bath shall be in order of quantity :

1) Copper anodes, H_2SO_4, and copper sulphate
2) Brightener and additive.


Metal copper
1 000 kg
Anodes
+
salts
Deposit
920 kg
Maintenance
10 kg
Drag out
60 kg
TOTAL WASTE 70 KG
or 7 %
H_2SO_4
1 000 kg
Maintenance
60 kg
Drag out
940 kg
TOTAL WASTE 1,000 KG
or 100 %

Copper sulphate is consumed when there is a difference between the anodic dissolution and the deposit + wastes which causes a decrease in the copper content in the bath.

This is the case when there is a lack of balance in the anode/cathode ratio or when there are large amounts of waste by drag out.

6.2.5. Control techniques

ECO rinse (therefore static recovery rinse)	+	+
Ion exchangers (therefore static recovery rinse)	+	+
Electrolysis (therefore static recovery rinse)	+	+
Decreaserate in copper losses by drag out............	80 %	90 %

Rinse waters may be concentrated by ion exchangers prior to they be electrolysed.

Operation may be series cascade rinse-ion exchange resins-electrolyser. Metallic recovered copper may be reintroduced into the plating bath in the form of anode. Recovered copper sulphate may be reintroduced into the plating baths thanks to a new application of ion exchangers.

A.2.6. Case study : Acid copper plating in the frame

Plating bath : 9.6 m^3, 200 to 250 g $CuSO_4 (H_2O)$/l,
50 to 70 g H_2SO_4/l
50 to 100 g NaCl/l

Drag out : 2.51 l/hr or 0,115 l/m^2

Copper losses : 7 % : 5.1 % rinsing
1.94 % miscellaneous

Provision :

Acid copper plating bath : 55 g Cu/l
Reclaim rinse (circulating through an electrolytic cell) :15 g Cu/l
Straining (13.5 g Cu/l)
Acid cleaning bath (2 g Cu/l)
Rinse (< 15 mg Cu/l)

The solution from the reclaim rinse and from straining is first used to balance the copper plating bath.

Electrolytic cell : 75 A 2.5 Volts (0.6 A/dm^2)

Theorical recovery : 82.5 g Cu/hr

Current efficiency : 90 to 95 %

Copper losses : 2.8 % : 0.8 % rinsing
2.0 % miscellaneous.

Electrolytically recovered copper is reintroduced into the plating bath in the form of anode.

Decrease in copper pollutant flow : TOTAL : 60 %
in rinses : 84.3 %

Miscellaneous losses which are now important, are discontinuous and can be controlled.

The recovery efficiency could have been more important if the electrolytic tank were not too small.

A.2.7. Technical variants

. Electrolytic polishing of the substrate upon steel and the coppers, but increase in the nickel deposit thickness ;

. Improvement in the operations of cyanided alkaline copper and nickel chromium plating upon zamac.

A.3. WATTS NICKEL PLATING

- Electrolytic treatment
- Hot bath

A.3.1. Utilization

The electrolytic deposit of nickel is used mainly in two applications :

1) Anticorrosion and decoration :
   it is the pair nickel + chromium with or without undercoat ;

2) Decoration :
   Nickel is a finish : especially for the nickel plating of small loose pieces in the drum.

NOTE : this deposit takes place :

- either in the frame,
- or in the drum.

Of all the coatings, the pair nickel + chromium are certainly the most widely used for their protective and decorative qualities.

The nickel deposit issued to protect the metals from corrosion, as it has a higher potential than steel. The protection is mechanical and the coating must not have any porosity.

An intermediate undercoat consisting of cyanided alkaline copper is often applied (see copper).

Due to the fact that nickel deposits alone are not appreciated because of their yellowish sheen, they are coated with a thin chromium layer, which has a much nicer bluish sheen.

A.3.2. Main characteristics

The most widely used nickel plating baths contain simple nickel salts of the Watts type.

The standard composition is the following :

- nickel sulphate : 300 g/l
- nickel chloride : 60 g/l
- boric acid : 50 g/l
- additives

The anodes are anodes which are soluble in nickel.

Nickel sulphate serves as a reserve for nickel ions.

Nickel chloride brings the necessary chloride ions to the anodic dissolution of nickel.

Boric acid serves as a buffer to maintain the pH.

Generally, the nickel salts of the bath serve as buffer between the nickel coming from the anodes and the nickel which is deposited on the slugs.

The simplified reactions are as follows :

$$\overset{\underline{\text{Anode}}}{Ni} \longrightarrow \overset{\underline{\text{Bath}}}{Ni^{++} + 2e^-} \longrightarrow \overset{\underline{\text{slug}}}{Ni}$$

At the cathode, there is always a hydrogen emission at the same time as the nickel deposit.

$$2H^+ + 2e^- \longrightarrow H_2 \nearrow$$

At the anode, when the anodic surface is light, oxygen may be released.

$$H_2O \longrightarrow 2H^+ + 2e^- + \frac{1}{2} O_2 \nearrow$$

Brightener nickel bath

Composition in g/liter :

. Hydrated nickel sulphate : 250 to 350
. Hydrated nickel chloride : 50 to 60
. Boric acid : 40 to 50
. Penetrating additives : depending on supplier and use
. Levelling additives
. Brighteners.

pH electrometric : 3.5 to 4.5

Temperature : 50 to 70 ° C

Current density : 1 to 10 A/dm^2

Deposit velocity : 60 microns/hour at 5 A/dm^2 electrolytic nickel, depolarized - purity 99.5 -bagged

Anode/cathode ratio : 2/1

Ampere/liter ratio : 1/1

Agitation : mechanical or air blown

Filtration : continuous on activated carbon

The anode efficiency of the bath is higher than the cathode efficiency and they are, respectively : 98 and 96 %.

A.3.3. Location of the bath in the chain

upon steel or brass	upon zamac	upon zamac in the drum
- Chemical degreasing	- chemical degreasing	- Chemical degreasing
- Rinsing		
- Electrolytic degreasing	- Ultra sonic degreas.	- Rinsing
- Rinsing	- Electrolytic degreas.	
- Acid depassivation	- Rinsing	- Depassivation
- Rinsing	- Acid depassivation	- Rinsing
- Cyanided coppering	- Rinsing	- Cyanided coppering
- Rinsing	- Cyanided coppering	- Rinsing
- Acid rinsing	- Rinsing	- NICKEL PLATING
- Acid coppering	- NICKEL PLATING	- Rinsing
- Rinsing	- Rinsing	
- Acid depassivation	- Chromium plating	
- Rinsing	- Rinsing	
- NICKEL PLATING		
- Rinsing		
- Chromium plating		
- Rinsing		

The term "rinsing" designates the "rinsing function" and implies several tanks.

A.3.4. Simplified substance balance

The wastes generated during the operation of this type of bath are the following :

Wastes by drag out :

Drag out in the rinsings of a solution volume having the same characteristics as the deposit bath.

Maintenance wastes :

They include :
- liquid wastes by restoring the filters of the continuous filtration.

- liquid wastes generated during manipulation of the bath to perform curative or preventive treatments to eliminate impurities (treatment of activated carbon, iron , for example, etc...)
- metal waste caused by selective purification electrolysis of parasitic metals (zinc, copper).

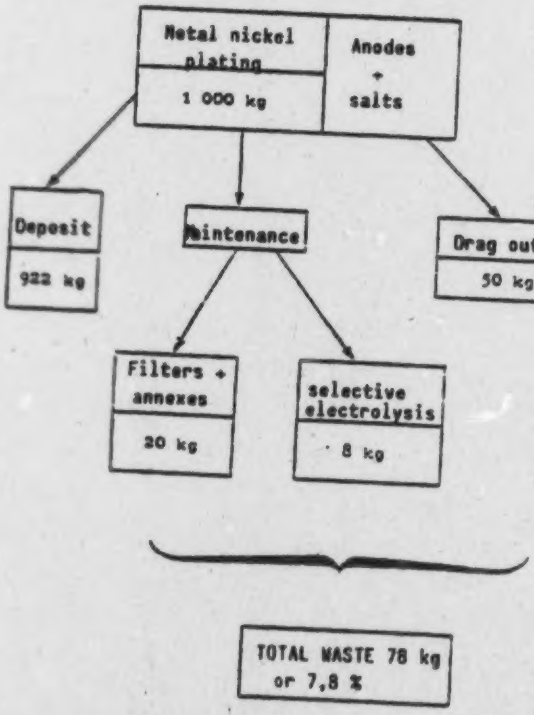
The largest wastes are in the following order :

1) Drag out losses

2) Maintenance wastes.

The basic products consumed during the operation of the nickel plating bath shall be :

- nickel anodes
- nickel salts ($NiSO_4$ $NiCl_2$)
- boric acid
- purification products


Metal nickel plating
1 000 kg
Anodes + salts
Deposit
922 kg
Maintenance
Drag out
50 kg
Filters + annexes
20 kg
selective electrolysis
8 kg
TOTAL WASTE 78 kg
or 7,8 %

A.3.5. Control techniques

. Straining	+
. Static recovery rinse	+
Decrease rate in nickel losses in drag out....................	98 %

In some cases, the plating bath losses may be balanced by the way of a static rinse, but direct losses recycling occurs to be prohibited because of the decomposition of some organic additives.

Concentration and purification of the rinse waters or (and) nickel recovery is possible applying :

- reverse osmosis and other membrane techniques (concentration of the rinse waters) ;
- ion exchangers : concentration (cationic) and purification (anionic) of the rinse waters.

The concentrated purified solution may be used to balance the plating bath :

- evaporation (concentration of the rinsing waters)
- end-of-pipe treatments :

  ·The introduction of nickel diethylthiocarbamate into the nickel plating bath insolubilizes impurities (zinc, copper, iron) as metallic salts which can be seperated by filtration (diethylthiocarbamate costs about 50 F/kg)

A.3.6. Case study : nickel plating upon steel in the drum

Plating bath : 9.75 m3, 90 g Ni/l
Drag out : 2.28 l/drum or 0.088 l/kg
Straining above nickel plating bath : 20 sec.
Nickel losses : 33.6 % : 32.08 % rinsing
1.52 % miscellaneous.

Provision :

Nickel plating bath
Static Rinse 1
Static Rinse 2
Acid Rinse
Running Rinse

Losses due to evaporation of the hot nickel plating bath are balanced with the solution from the two static rinses.

Nickel losses : 6.86 % : 4.73 % rinsing
2.13 % miscellaneous

Decrease rate in nickel losses : TOTAL : 85.5. %
in rinses : 89.5 %

Nickel plating upon zamac in the drum

Plating bath : 4.75 m3, 90 g Ni/l

Drag out : 1.15 l/drum (0.076 l/kg)

Straining : 20 sec. (nickel station) 10 sec. (rinsing)

Nickel losses in drag out : 324.72 kg/year

Provision : The same as for nickel plating upon steel.

Nickel pollutant flow was reduced by 98.64 % in rinses.

A.3.7. Technical variants

- Nickel-iron deposit
- Low concentration bath.

- Electrolytic tratment
- Hot bath

A.4.1. Utilization

Decorative electrolytic chromium plating is used as a finishing coat upon nickel deposit for the following reasons :

- appearance (color)
- anticorrosion (pair Ni–Cr)
- antiabrasion (Cr hardness)

NOTE : This deposit takes place in the frame for 98 % of the cases. Chromium plating in the drum requires a specialized technique and means.

Until now, chromium deposits are mainly obtained from solutions composed of hexavalent chromium, such as chromic acid CrO_3.

Catalytic agents are required to achieve deposits in a hexavalent chromium medium. Catalysers used are sulphate anions, fluosilicate, fluoborate or fluoride, as well as the presence of trivalent chromium.

The anodes are insoluble anodes with load alloy, because chromium anodes produce such a high trivalent chromium content that it is considered as an impurity.

Standard baths have the following composition :

- CrO_3 : 250 to 300 g/l
- Catalyst : 1 %

A.4.2. Standard decorative chromium plating bath

- CrO_3 : 250 to 300 g/l
- SO_4^{--} : 1 %
- Cr_3 :

Possible impurities : Fe, Cu, Zn, Al
Sum impurities + Cr_3 : 10 g/l

Temperature : 30 to 40° C

Current density : 8 to 25 A/dm2

Efficiency : 10 to 17 %

Deposit velocity : 8 microns/hr to 15 A/dm2

Anode/cathode ratio : 1

Ampere/liter ratio : 1

The chromium deposit is carried out with gas emissions :

- oxygen containing anode (insoluble anode)
- hydrogen containing cathode (very poor cathodic efficiency (20 %) entraining chromic acid vesicules in the suction.

A.4.3. Location of the chromium plating bath in the technological chains

As this is a finishing treatment, the chromium plating bath takes place at the end of the treatment chain as follows :

- chromium plating
- rinsing
- hot rinsing or water-proofing
- exit

(see preceding series)

A.4.4. Simplified substance balance

The following wastes are generated by the operation :

Drag out wastes :

Drag out in the rinsings of a solution volume having the same characteristics as the plating bath.

Maintenance wastes :

These are volume wastes during bath manipulation to perform tank to tank maintenance.

Wastes in steam (air) :

Account taken of the high volume of gas emission, there is a liquid entrainment having the characteristics of the chromium bath in the air sucked above the bath.

Degradation wastes :

Reduction of Cr^6 into Cr^3 by unbalancing the anode and cathode phenomena (O_2 - H_2).

The largest quantities of wastes are in the following order :

1) Drag out wastes

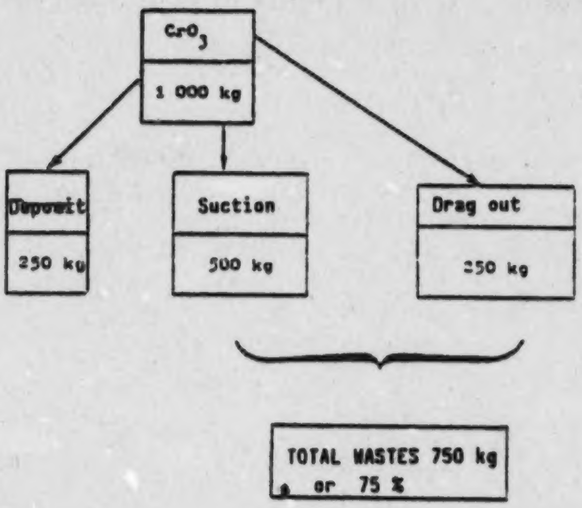
2) Wastes in steam

3) Wastes from maintenance

4) Degradation.

The consumption of basic products includes mainly chromic acid at the level of :

300 to 400 g CrO_3/kilo-ampere/hour


CrO_3
1 000 kg
Deposit
250 kg
Suction
500 kg
Drag out
250 kg
TOTAL WASTES 750 kg
or 75 %

A.4.5. Control techniques

Straining	+	+	+
ECO rinse (therefore static recovery rinse)	+	+	+
Evaporation (therefore ion exchangers and cascade rinses)		+	+
Electrodialysis (therefore evaporation)			+
	70 %	98 %	98 %

Rinse waters are either concentrated or purifyed on ion exchange resins.

By evaporation, rinse waters are concentrated and sucted Cr O_3 is recovered.

Electrodialysis purifies the concentrated effluents prior to their recycling into the plating bath.

A.4.6. Case study : Chromium shop

Chromic acid recovery in the three stations :

- electrolytic chromium plating
- chromic passivation upon cadmium (2 stations)
- chromium finishing upon zamac.

Electrolytic chromium plating :

Up to 50 % of drag out losses are recovered by managing an ECO rinse.

Chromic passivation upon cadmium

(in the frame and in the drum)

Cr O3 Annual losses

CHAIN	SPENT BATHS	RINSES
frame	580 kg	12.5 kg
Drum	510 kg	63 kg
SUM	1 090 kg	75.5 kg

Provision :

- brightening in a 100 g Cr 0_3/l solution
- passivation in a diluted Cr 0_3 solution.

Continuous purification of the two baths by the way of ion exchangers.

Evaporation of the rinse after brightening to concentrate and reintroduction into the purification circuit, therefore into the concentrated bath.

Recovered Cr 0_3 : 6 950 kg/year

Cr 0_3 losses : 150 kg/year

(rinse after chromic passivation)

Previous costs (1979) :

- Purification and recycling of a chromic passivation bath	182,300 FF
- Evaporator	315,500 FF
- Purification of diluted passivation solutions	160,000 FF
- Studies and tests	68,000 FF
TOTAL..............	725,800 FF

A.4.7. Technical variants

Chromium plating bath containing low concentration of $Cr\ 0_3$

These baths are used more and more and operate with low concentrations ranging between 150 and 200 g/l $Cr\ 0_3$ with excellent results.

Baths with 50 g/l $Cr\ 0_3$ are at present being studied in laboratory research.

Trivalent chromium plating baths

This type of bath is being used in industry in France since 1977. Three points distinguish Cr3 from Cr6 :

- The Cr^{+3} bath must be maintained at an ambient temperature rather than being raised to 40° as in the case of Cr^{+6}. Temperature exchangers are required to accomplish this effect : the energy required, however, to maintain the Cr^{+3} bath at 20° C is considerably less than the energy required to maintain the Cr^{+6} at 40° C.

- It follows from the first point that there is no emission of toxic steam in the case of Cr^{+3}, whereas in the case of Cr^{+6} an appropriate collecting facility must be provided for the escaped steam.

- The Cr^{+3} bath is easier to perform : the current can be shut off during the electrolysis without any disruption. In the case of Cr_{+6}, if the current is accidentally shut off, the slugs must be polished. This sometimes occurs for 10 minutes during the electrolysis of chromium. The use of Cr^{+3} permits, then, a considerable decrease in the rate of losses.

Even if it is possible to use trivalent chromium for the deposit procedures, hexavalent chromium is always necessary for the oxidizing function (anodic oxidation, zinc and cadmium passivation, chromatizing on zamac, phosphatation, decoppering, chemical oxidation...) where most of the chromium consumed by the metal finishing industry is utilized.

Deposit of alloys substituting the chromium coating

These are the Sn-Co alloys which have appearance and anticorrosion characteristics similar to the standard chromium deposit.

This bath contains low concentration of metals (4 to 6 g/l) and needs no suction.

A.5. THICK CHROMIUM PLATING

. Electrolytic treatment

. Hot bath

A.5.1. Utilization

Due to its hardness, cristallization and nature, thick chromium is used for the following applications :

1) Mechanical	friction abrasion
2) Anticorrosion	chemical atmospheric combined
3) Special	anti-adhesive

The only difference with decorative chromium is that the thickness deposited is much greater.

Several tens of microns for a few tenths of microns for the decorative chromium.

The slugs remain in the bath much longer, sometimes for several hours.

This deposit is applied only in the frame.

A.5.2. Standard hard chromium plating bath

Composition :

- CrO_3 : 250 g/l
- SO_4^{--} : 2.5 g/l
- Cr^{3+} : about 1 g/l at he onset (low concentration required) sum impurities < 15 g/l, $Cr3 < 7$ g/l

Impurities possible : Fe, Cu, mainly

Temperature : 50 to 55° C

Current density : 20 to 50 A/dm2

Efficiency : 15 to 20 %

Anode/cathode ratio : 1

Ampere/liter ratio : 1

Anodes lead-antimony, lead-tin, lead-tin silver, steel, platinized titanium.

A.5.3. Location of the bath in the chain

The electrolytic technique of thick chromium plating is relatively simple, as the deposit is generally applied directly upon the substrate.

Furthermore, account taken of the chemical nature of the bath and of the nature of the slug treated, the technological chain is reduced to its simplest expression.

It is in the form :

- manual degreasing
- pickling - chromium plating
- rinsing

The term "rinsing" designates the "rinsing function" and implies several tanks.

A.5.4. Simplified substance balance

The following wastes are generated during the operation :

Drag out wastes :

Drag out in the rinsings of a volume of solution having the same characteristics as the plating bath.

Maintenance wastes :

These are volume wastes during the manipulation of the bath to do tank to tank maintenance.

Wastes in the steam (air) :

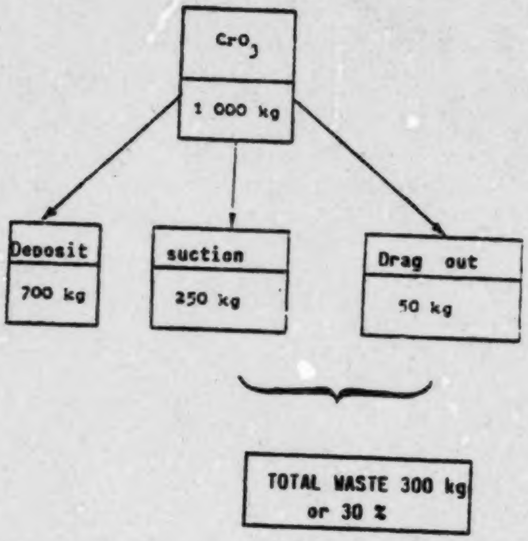
Account taken of the high volume of gas emission, there is a liquid entrainment having the characteristics of the chromium plating bath in the air sucked above the bath.

Degradation wastes :

Reduction of Cr6 into Cr3 by unbalance in anode and cathode phenomena (O_2 -H_2).

NOTE : If the slugs remain in the bath longer, drag out wastes shall be less than for decorative chromium plating. Wastes in the steam shall increase.

The product consumed is chromic acid at the level of :



A.5.5. Control techniques

. Straining	+	+
. Static recovery rinse (induces ion exchange)	+	
. Electrodialysis (induces static recovery rinse)		+
Decrease rate in $Cr\,O_3$ losses in drag out and suction.................	95 %	95 %

The plating bath is warmer for thick chromium plating than for decorative plating, and suction losses (the same components and the same concentrations as in the plating bath) are relatively more important than drag out ones, therefore the evaporation of the effluents to concentrate becomes unnecessary.

A.5.6. Case study : thick chromium plating chain

CrO3 losses : - suction : 30 %

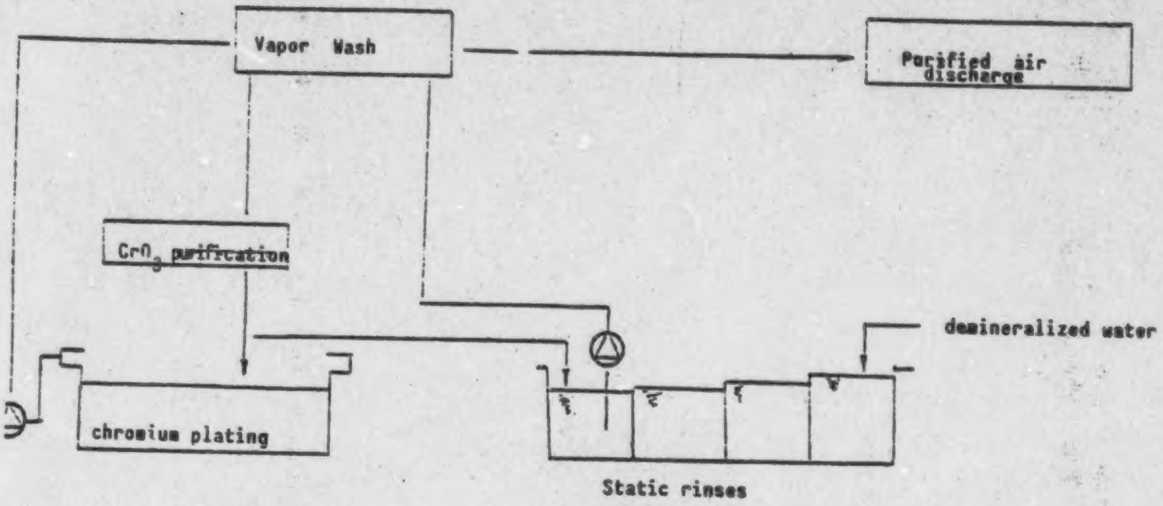
- rinse : 3 %

Provision : Cr03 direct recovery from steam and rinse waters by managing static recovery rinses which are used to purify gas.

CrO3 losses : 0 %

Reduction of the pollutant flow : 100 %

Neither disposal to air nor to water



A.5.7. Technical variants

A.5.7.1. Chemical nickel

This is an alloy deposit Ni-P or Ni-B, which has after heat treatment a high degree of hardness characteristics which may be combined to the anticorrosion qualities of the nickel coat.

Due to the nature of the alloy, the deposit is used in some applications for its friction qualities.

A.5.7.2. Metallization by projection, by plasma

This is the projection upon the substrate of alloys, oxides, pure bodies having mechanical properties which are quite special, both from the point of view of hardness, resistance (chemical) and from the point of view of heat resistance.

Ion deposition and cathodic pulverization are absolutely non polluting processes because they do not use any chemical substance.

Vacuum metallization is particularly developped in Japan and takes an increasing place in the U.S.A. and in Europe.

Ion deposition is adopted by manufactures whose products are expansive and need coating characteristics which cannot be satisfied with any other deposition method.

In any case, investments are expansive, but these processes are non pollutant ones, the deposition works faster and the bulkiness is not so important as for standard methods.

Moreover, a number of treatments prior to painting become unuseful by using these technologies (see "Vacuum evaporation in A.12)

A.6. CYANIDED ZINC PLATING

- Electrolytic treatment
- Cold bath

A.6.1. Utilization

Zinc is widely used in industry for the protection of steel from corrosion.

- by projection
- by hot dipping = galvanization
- by electrolysis.

Zinc is a metal similar to cadmium from the chemical point of view ; its potential is lower than that of steel. As a result, a zinc coat is protective, even if the deposit is porous.

The electrolytic zinc deposit always undergoes a supplementary protective finish in hexavalent chromium solutions. See chromic passivation.

Only a few years back, the only baths used for the deposit of electrolytic zinc were cyanided baths containing about 100 g/l $NaCN$.

For reasons which are essentially ecological, and even though the standard cyanide zinc plating is still widely used, the following zinc plating baths may be found on the market :

- Cyanided average zinc.......................$NaCN$ 20-30 g/l ; Zn 10-15 g/l
- alkaline zinc without cyanide...............Zn approx. 10-15 g/l ; $NaOH$ 80-100 g/l
- zinc acid...................................Zn 40 g/l ; $NH_4 Cl$ - 200 g/l

A.6.2. Cyanided zinc plating bath

composition in g/l	BM standard
Zn metal	38
$CNNa$	100
$NaOH$	100
Sodium carbonate	60
Sodium sulfide	1 to 2
Brightener	depending on supplier

Temperature : optimum 20-35° C (15 to 45°)

Current density : 1.5 to 6 A/dm2

Current efficiency : 70 to 90 %

Deposit velocity : 60 microns/hour at 4 A/dm2

Anode nature : Zn in plates or purity sphere 99.9 steel when necessary or auxilliary anodes

Anode/cathode ratio : 1

Ampere/liter ratio : 0.5 to 0.7

Agitation : recommended, brings better performance

Filtration : recommended.

A.6.3. Location of the bath in the chain

ZINC PLATING IN DRUMS	ZINC PLATING FRAMES	ZINC PLATING FRAMES
Pickling	Chemical degreas.	Chemical degreas.
Rinsing	Rinsing	Electrolyctic degreas.
Electrolytic degr.	Pickling	Rinsing
Rinsing	Rinsing	Pickling
ZINC PLATING	Electrolyt. degr.	Rinsing
Rinsing	Rinsing	Neutralization
Acid polishing	ZINC PLATING	Rinsing
Blue passivation	Rinsing	ZINC PLATING
Rinsing	Blue passivation	Rinsing
Yellow passivation	Rinsing	Acid polishing
Rinsing		Yellow passivation
		Rinsing

The term "rinsing" designates the "rinsing function" and implies several tanks.

A.6.4. Simplified substance balance

Wastes generated during the operation of this type of bath are the following :

Drag out wastes :

Drag out in the rinsings of a volume of solution having the same characteristics as the deposit bath.

Wastes from maintenance :

They include : - liquid wastes by the restoration of filters of the continuous filtration ;

- liquid wastes generated during bath manipulation to perform curative or preventive treatments to eliminate impurities (activated carbon treatment, for example).

Degradation wastes :

Anode phenomena generates a degradation of the ion CN^- into sodium carbonate, the high concentration of which may be detrimental to the functioning fo the bath.

NOTE : the greatest wastes are :

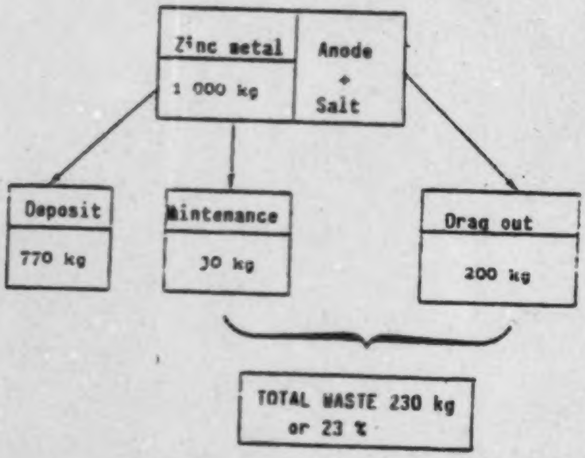
- drag out
- degradation.

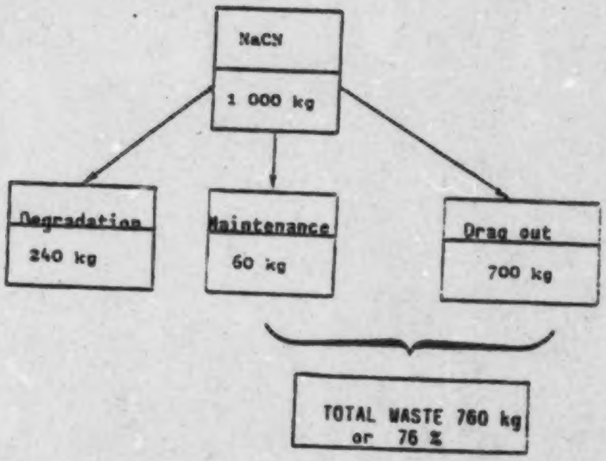
Product consumption of this type of bath shall be in order of amount :

1) Na CN + zinc anodes
2) Other bath constituents + additives.

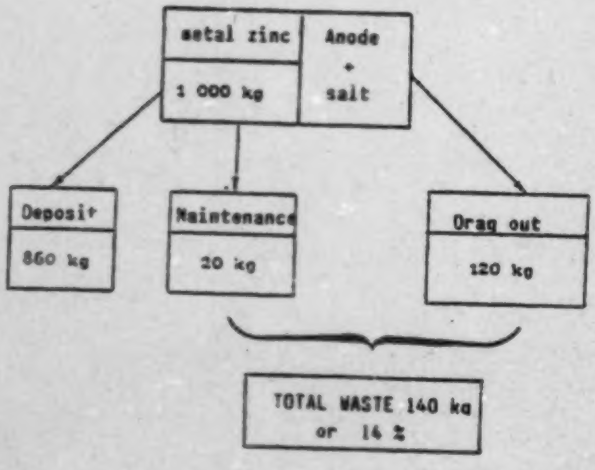
ZINC PLATING DRUMS

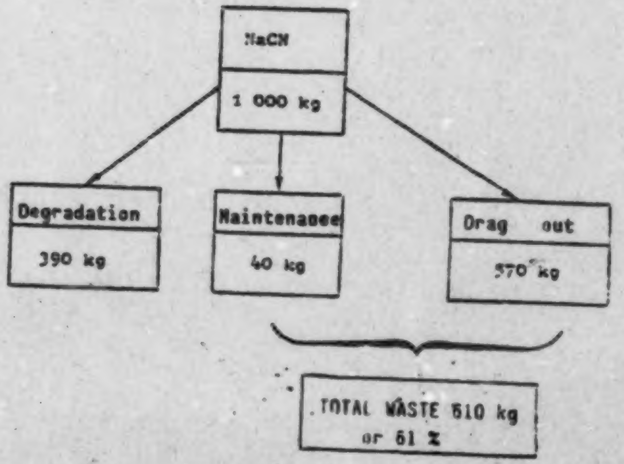
High Cyanide Baths


Zinc metal
1 000 kg
Anode + Salt
Deposit
770 kg
Maintenance
30 kg
Drag out
200 kg
TOTAL WASTE 230 kg or 23 %


NaCN
1 000 kg
Degradation
240 kg
Maintenance
60 kg
Drag out
700 kg
TOTAL WASTE 760 kg or 76 %

Medium Cyanide Baths


metal zinc
1 000 kg
Anode + salt
Deposit
860 kg
Maintenance
20 kg
Drag out
120 kg
TOTAL WASTE 140 kg or 14 %


NaCN
1 000 kg
Degradation
390 kg
Maintenance
40 kg
Drag out
570 kg
TOTAL WASTE 610 kg or 61 %

A.6.5. Control techniques

· Straining	+	+	+
· ECO rinse (therefore static recovery rinse)	+	+	+
· Electro lysis (therefore static recovery rinse)		+	
· Evaporation (induces static recovery rinse)			+
Decrease rate in drag out losses.......	70 %	80 %	98 %

Electrolysis destroys a part of cyanides and recovered metallic zinc may be reintroduced into the plating bath in order to balance drag out losses.

A.6.6. Case study : zinc plating in the frame and in the drum

Zinc plating bath : 3 600 l, 14 g Zn/l

Drag out : 0.65 l/drum

Losses : 13.4 % from added zinc.

Provision :

Zinc plating bath —— 2
ECO rinse ———— 1 3
rinse 4

The balance of the zinc plating bath is done with the ECO rinse solution, that rinse being supplied with raw water.

Annual losses : 5.28 % in added zinc.

Pollutant flow of zinc, NaCN and NaOH in the rinses have been reduced by 64 %.

A.6.7. Technical variants

2.6.5.1. Zinc coating by thermocompression process 3M

May be used upon small loose slugs with little decorative value.

The deposit is executed by the glass ball effect upon the slugs mixed with an additive containing zinc powder.

The preparation and finishing phases of the zinc deposit are identical to those of electrolytic zinc.

The advantage of the process lies in the fact that the efficiency of producing metal zinc is 100 % and that the other products used are not very toxic.

2.6.5.2. Zinc based coating by ACROLYT process

The deposit complex is applied like a painting, i.e. :

- coating by immersion
- drying
- firing

The phase of surface preparation is standard and there is no chromium finishing.

Except for the phase of surface preparation, the process does not generate liquid effluents.

As their coatings are dull, these untraditional processes apply to slugs which do not have to be decorative and to loose, small and medium sized slugs. The coatings applied do not become brittle and are thus used upon slugs working under stress. Their anticorrosion properties are good.

These processes generate less liquid effluents than the standard electrolytic zinc plating.

A.7. ACID ZINC PLATING

.electrolytic treatment
.cold bath

A.7.1. Utilization

As it has the same applications as the standard cyanided zinc plating, this kind of zinc plating was developped mainly to eliminate the use of sodium cyanide.

Besides this advantage, acid zinc plating has several interesting qualities, namely :

- shiny deposit
- higher cathode efficiency than the cyanided bath ; hence the deposit is not as brittle
- smoothness

This bath is used in the frame or in the drum.

A.7.2. Acid zinc baths

There are at present two kinds of baths :

- ammonium chloride bath
- potassium chloride bath

The potassium chloride bath was developped to prevent the use and waste of NH4.

Composition :

- Metal zinc : 30 to 50 g/l
- Cl : 130 to 150 g/l
- Boric acid : 15 to 150 g/l
- Brighteners :
- pH : 5 to 6

Temperature : 20 to 30° C
Current density : 1 to 5 A/dm2
Deposit velocity : 60/hour at 4A/dm2
Anode type : Pure zinc
Anode/cathode ratio : 3
Agitation :
Filtration : continuous

A.7.3. Location of the zinc plating bath in the technological chains

This process has about the same position as the cyanided zinc bath, with the exception that the preparation prior to deposition (degreasing-pickling) shall be more developped to compensate the cleaning characteristic of sodium cyanide.

Accordingly, the preparation series prior to acid zinc shall be more elaborate and shall approximate the prepartation series prior to nickel-chrome.

Example :

- Chemical degreasing
- rinsing
- pickling
- rinsing
- electrolytic degreaser
- rinsing
- acid depassivation
- rinsing

- ACID ZINC PLATING

- rinsing
- acid brightener
- blue passivation
- rinsing
- hot rinsing

A.7.4. Simplified substance balance

Wastes generated during the operation of this type of bath are the following :

Drag out wastes :

Drag out in the rinsings of a volume of solution having the same characteristics as the deposition bath.

Wastes from maintenance :

They include :

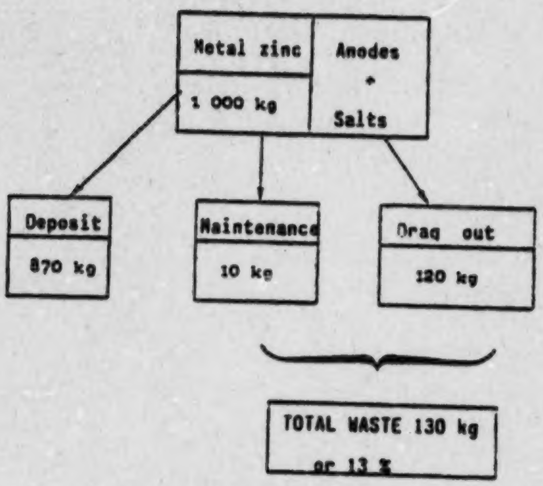
- liquid wastes by repairing the filters of the continuous filtration,

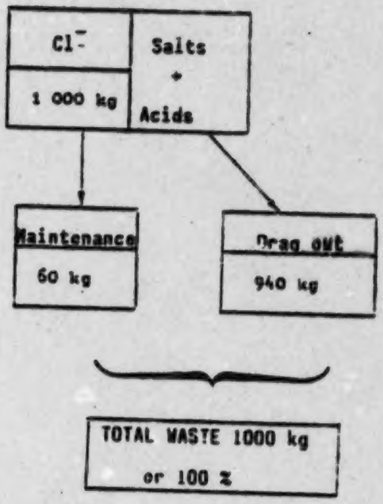
- liquid wastes generated during bath manipulation to perform curative or preventive treatment to eliminate impurities (activated carbon, for example).

The greatest wastes are : drag out.

Products consumption of this type of bath shall be of the constituant products of the bath :

- metal zinc
- salinity
- additional agents (brighteners + penetrants)


Metal zinc
1 000 kg
Anodes
+
Salts
Deposit
870 kg
Maintenance
10 kg
Drag out
120 kg
TOTAL WASTE 130 kg
or 13 %


Cl$^-$
1 000 kg
Salts
+
Acids
Maintenance
60 kg
Drag out
940 kg
TOTAL WASTE 1000 kg
or 100 %

A.7.5. Control techniques

. Straining	+	+
. ECO rinse	+	+
. Electrolysis	+	
. Electrodialysis		+
Decrease in drag out losses........	80 %	80 %

Metal recovered zinc in electrolysis is valorized as in the form of anode. Electrodialysis concentrates and purifies rinse waters which are recycled into the plating bath to balance the drag out losses.

A.7.6. Technical variants

Refer to cyanided zinc plating.

A.8. CYANIDED CADMIUM PLATING

- Electrolytic treatment
- Cold bath

A.8.1. Utilization

Cadmium is a metal having properties similar to those of zinc. It is used for its anticorrosion properties upon steels because its dissolution potential is less than for iron in the electro-chemical corrosion phases : this results in iron protection even if the deposit is not continuous.

Its properties of protection from corrosion may be increased by chemical chromatizing.

Cadmium is less widely used than zinc (cost) but it is used because of its special properties (weldability), especially in the field of electronics.

Il should be pointed out that it is prohibited (in France) to apply this product for any food usage.

A.8.2. Bath composition

Baths used in the industry are usually baths with high cyanide contents having a composition which may vary as follows :

- metal cadmium.........	15 to 20 g/l
- sodium cyanide........	90 to 120 g/l
- soda..................	30 to 150 g/l

Low metal concentrations are recommended for the process in the drum where drag out wastes are high.

The cyanided cadmium bath works with soluble anodes containing cadmium, either in the form of plates or in the form of balls in iron ball-carrying baskets.

This treatment may be performed in the frame or in the drum.

A.8.3. Location of the cadmium plating baths in the technological chains

It is similar to the cyanided zinc plating bath.

CADMIUM PLATING DRUMS	
Chemical degreasing	Electrolytic degreasing
Rinsing	Rinsing
Pickling	Pickling
Rinsing	Rinsing
Neutralization	
Rinsing	
CADMIUM PLATING	CADMIUM PLATING
Rinsing	Rinsing
Yellow passivation	Acid brightener
Rinsing	Yellow passivation
Hot rinsing	Rinsing

A.8.4. Simplified substance balance

Wastes generated during the operation of this type of bath are the following :

Drag out wastes :

Drag out in the rinsings of a volume of solution having the same characteristics as the depositon bath.

Wastes from maintenance :

They include :

- liquid wastes produced while replacing filters of the continuous filtration,

- liquid wastes generated during bath manipulation to perform curative or preventive treatments to eliminate impurities, (activated carbon, for example).

Wastes by degradation :

The anode phenomena generates a degradation of the ion CN^- into sodium carbonate, high concentrations of which may be detrimental to the operation of the bath.

The largest amounts of wastes are :

- drag out
- degradation.

Product consumption of this type of bath shall be in order of quantity :

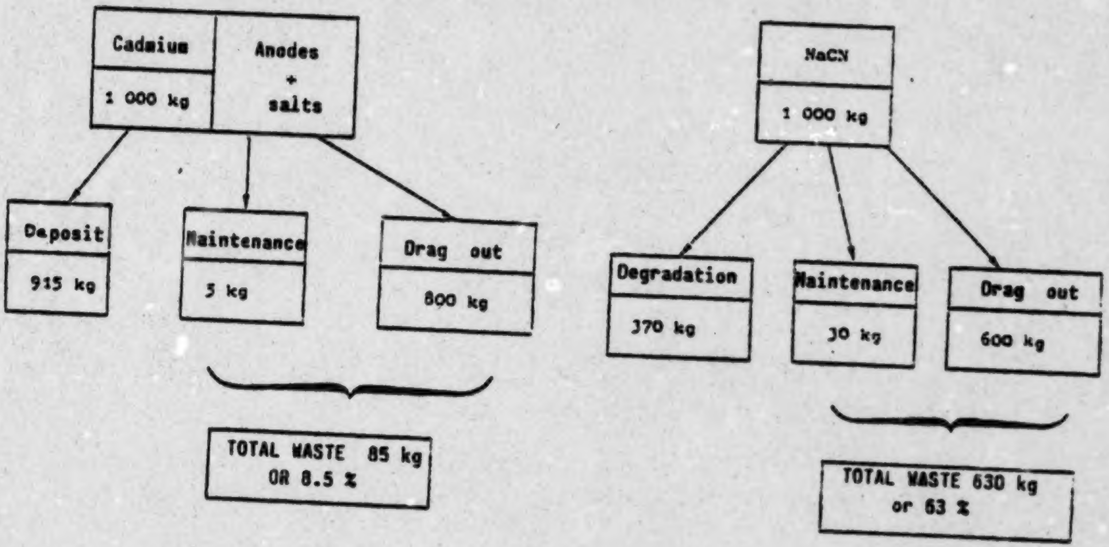
1) NaCN + cadmium anodes
2) Other bath components + additives.

The content in cadmium must remain practically constant by regulating the anodic and chemical dissolution of the anodes which compensate wastes by drag out and deposition.

Frequent additions of cadmium salts (cadmium oxide) indicate a poor operation or excessive drag out into the rinsings.

The bath serves as a vehicle for metal Cd and the double cyanide is dissociated in two phases to form the metal deposit upon the cathode.

CADMIUM PLATING IN THE DRUM


Cadmium
1 000 kg
Anodes + salts
Deposit
915 kg
Maintenance
5 kg
Drag out
800 kg
TOTAL WASTE 85 kg OR 8.5 %
NaCN
1 000 kg
Degradation
370 kg
Maintenance
30 kg
Drag out
600 kg
TOTAL WASTE 630 kg or 63 %

A.8.5. Control techniques

The same techniques as for cyanided zinc plating.

A.8.6. Case study : cadmium plating in the drum

Plating bath : 900 l , 30-32 g Cd/l, 120 g NaCN/l

Drag out : 0.36 l/drum (one drum : 15 kg sludgs, 2 m2)

Losses : 18.5 % of added cadmium.

Provision :

Cadmium plating bath ←		3
ECO rinse 1	2	4
ECO rinse 2	1	5
Rinse		6

The plating bath is balanced with solution from ECO rinse 1 which is supplied with ECO rinse 2 which is supplied with raw water.

Annual losses : 2.93 % of added cadmium.

Cadmium and sodium cyanide pollutant flow in the running rinse was reduced by 86.7 %.

A.8.7. Technical variants

Except for problems of welding where cadmium is indispensable : see zinc plating and technical variants of zinc plating.

The substitution of cadmium by zinc has been accomplished in a few cases. This substitution is encouraged by the cost of cadmium which is 15 to 30 times higher than for zinc. The main obstacles to new substitutions being developped are :

- poor friction resistance of the zinc deposit (main property in the screw cutting industry)
- poor electrical behaviour
- cadmium plating is held better by steel than zinc plating, after special dipping.

A.9 CHROMIC PASSIVATIONS

- Chemical treatment
- Cold bath

A.9.1. Utilization

This is a case of a surface conversion treatment of a substrate which increases the anticorrosion efficiency of the slug and which has a decorative value.

By immersion in solution containing essentially hexavalent chromium, a coating of more or less complex chromates are formed on the surface of the substrate made of zinc, cadmium, aluminium, copper or brass and stainless steel.

The following characteristics are found upon substrates such as electrolytic zinc or electrolytic cadmium :

- white passivation
- blue passivation
- iridescent, yellow or chromatic passivation
- olive green passivation
- black passivation.

We shall discuss iridescent passivation upon zinc or cadmium.

A.9.2. Average characteristics

Composition :

- chromic acid	4 g/l
- sodium bichromate	7 g/l
- H_2SO_4	1 cm3/l
- HNO_3	0.1 cm3/l
- NaCl	1 g/l

Temperature : 20° C

pH : average 2

This type of treatment is performed both in the frame and in the drum. It is still possible to find in the industry so-called concentrated compositions containing several tens of grams/liter of hexavalent chromium.

A.9.3. Location of passivation in the technological chains

This is a finishing treatment, hence, it is always located at the end of the chain.

See zinc plating and cadmium plating.

A.9.4. Simplified substance balance

Wastes generated during the operation of this process are the following :

Drag out wastes :

Drag out in the rinsings of part of the bath having the characteristics of the treatment bath.

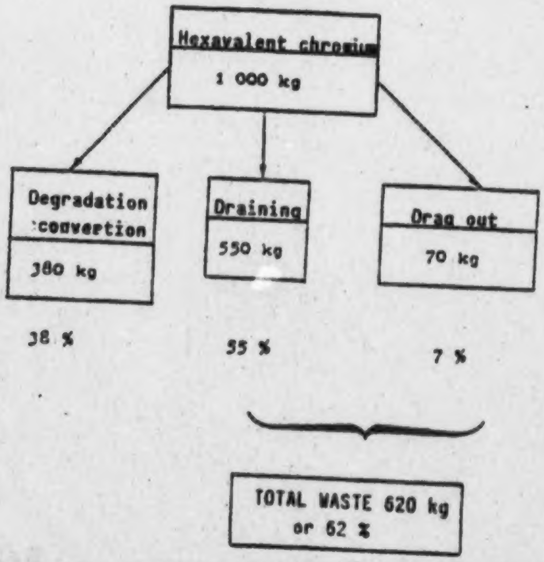
. Wastes by bath changes :

These wastes result from renovation of the degraded bath. The operation increases products resulting from the reaction of the chromatizing medium upon the zinc or cadmium substrate.

The frequency of bath changes can vary from several times a day to once a year.

Chromatization of the zinc surface accompanies a partial dissolution of the coating and a trivalent chromium formation in the solution. A degraded solution shall thus become low in active elements Cr6, acidity, various unions, by dissolution of substrate, conversion of Cr6 into Cr3 and by drag out. The solution shall increase in Cr3, thus in zinc or in cadmium and possibly iron, copper in small quantity coming from the slug or the transfer substances.

These shall comprise the essential elements of the pollution flux.



A.9.5. Control techniques

Straining	+
Ion exchangers	+
Decrease rate in CrO3 losses in drag out and draining........	98 %

The chromatic passivation bath is continuously purifyed on ion exchangers to prevent its draining.

Ion exchangers may be used too to concentrate hexavalent chromium contained in rinse waters.

A.9.6. Case study : zinc passivation

Acid zinc plating upon steel. Iridescent chromatic passivation.

Bath : 8 m3, 1.25 g Cr6/l, one draining a day

Cr6 losses : 62.3 % : 55.64 % spent baths
6.66 % rinsing

Provision :

Continuous purification of the chromatic passivation bath on ion exchange resins to prevent draining.

- Continuous circulation through ion exchange resins,
- Resin volume : 2 x 125 l
- Restoration : once a day

Cr6 losses : 15 % (rinsing)

Cr6 polluting flow has been reduced by 89.3 %

A.9.7 Technical variants

A.9.7.1 Utilization of passivation without hexavalent chromium requiring a finishing coat of polish to ensure an anticorrosion protection (upon zinc, aluminium, copper).

The type of chemical agents used has been kept secret until now by the manufacturers. In the present state of their development, their use results in a staining of the slugs which cannot be discolored. Furthermore, there is likely to be an increase in the flux of effluents.

Accordingly, the substitution of chromium in passivation baths after zinc plating is not widely practiced. A considerable decrease in the chromic oxide concentration of these baths, however, has often been performed successfully, (for example, from 150 g/l to 20 g/l). Present research in this field is orientated toward a dilution of baths rather than toward a substitution of chromium.

A.9.7.2. Utilization of ACROLYT type technique without finishing by any chromatic passivation. The coat ensures an anticorrosion protection equal to or even better than the couple :

Electrolytic zinc + passivation.

A.9.7.3. Substitution of the chromatizing by an electrolytic oxidation (mainly upon zamac)

A.9.8. Blue passivation

Blue passivation produces a lot of chromic effluents because of the very short life of passivation baths which is due to the reduction of hexavalent chromium into trivalent chromium and to the zinc dissolution. Restoring this bath is very difficult because nitric acid is present.

A substitution process, which industrial operation was sponsored by the Dutch Government, was found by the Dutch Organization of Scientific Applied Research (*). The treatment bath is based on trivalent chromium and sulfuric acid.

Laboratory investigations showed that :

- the same blue color could be obtained ;
- no difference in corrosion protection can be observed ;
- even high concentrations in solved zinc do not disturb the passivation process ;
- the bath life is longer than one month (probably 3 to 6 months) ;
- electrolytic precipitation of zinc in spent baths is possible because sulphuric acid is present.

(*) : Dutch Pattern 77.094.04 - 25/8/1977

A.10 COPPER PICKLING

- Chemical treatment
- Hot bath

A.10.1. Utilization

Copper pickling is used in industry for two applications with the same objective : removal of an oxide coat from the metal surface. This operation is required :

- either interoperations, the oxide coat being detrimental to the different processing phases (extraction, flattening, surface treatments, etc...)

- or at the final stage, the manufacture of the product as a decorative item.

The first application develops the most metal tonnage, as it involves the manufacturing of wire, pipes, copper plates of all sizes used in the electrical industry,sanitation, etc...

A.10.2. Procedure and characteristics

Pickling induces mainly the chemical dissolution of the oxides contained in the surface coat. The main products used are the following strong acides : H_2SO_4, HCl, HNO_3 alone or mixed, together with oxidizing salts, which are mainly CrO_3 or sodium bichromate.

The most widely used pickling process has a sulphuric acid base in a bath containing :

H_2SO_4 100 g/l, temperature 40 to 50° C

This pickling easily dissolves black oxide CuO by forming copper sulphate, while the red oxide Cu_2 results in the formation of metal copper in a powdery form. This copper remains on the surface of the pickled metal even after a standard dip rinse. This pulverulent coat is detrimental to the flattening or extraction operations which result (inclusions, tool wear). Furthermore, experience shows that this powdery copper is difficult to filtrate or settle with the standard means for obtaining good elimination results.

Techniques for eliminating this powdery copper have been researched. Two methods are used :

a) high-pressure spray rinsing, by mechanical effect detaches the loose coating ;

b) a second pickling in a highly oxidant medium allows for the solubilization of Cu^{++}. These baths contain a base of soda bichromate and its derivatives.

A.10.3. Location of pickling in the technological chains

Treatment series commonly encountered for the pickling wire in coils :

1) Pickling H_2SO_4 100 g/l, often several items (several m3)
2) High pressure spray rinsing (hand lance or automatic spray revolver in tank)
3) Neutralizing hot rinsing

Tubes are pickled : a) in bunches
b) in units, automatically

Wires are pickled : a) in coils
b) by automatic unwinding

Bars are pickled in bunches

A.10.4. Simplified substance balance

ITEM 1 – The dissolution of copper oxide in the pickling bath induces an increase in copper concentration. This copper content is maintained constant by continuous electrolysis of the bath where the copper is deposited upon cathodes with current densities ranging from 0.5 to 1.5 A/dm2. This technique is widely practiced and permits the recovery of several tons of copper in each plant.
The copper content in the pickling bath is thus stabilized between 10 and 20 g/l of copper in solution.
The content of sulphuric acid is maintained by constant additions. Hence, there are not effluent losses at this stage, except in the case of accidental losses or those resulting from annual tank cleaning (surface greases and copper powder at the bottom of the tank).

ITEM 2 – Spray rinsing : In this spray rinsing, we shall recover, in a continuous and diluted form, part of the pickling dragged out by the slugs into the rinsing tanks.
We have then :

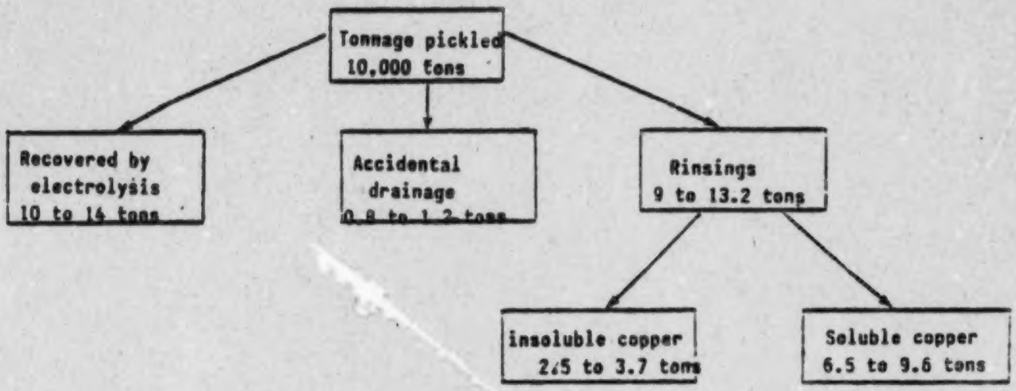
H_2SO_4
soluble Cu | in the ratio of the concentrated bath

We shall also recover the pulverulent copper detached from the slug surface by mechanical effect.
The pollution flux will then be :

H_2SO_4
Soluble Cu
Insoluble Cu
in diluted and continuous form.

ITEM 3 – Neutralizing hot rinse :
Moderately alkaline bath – no metal in solution
No rinsing and little drainage.

PICKLING OF COILS OF WIRE


Tonnage pickled
10,000 tons
Recovered by electrolysis
10 to 14 tons
Accidental drainage
0.8 to 1.2 tons
Rinsings
9 to 13.2 tons
insoluble copper
2.5 to 3.7 tons
Soluble copper
6.5 to 9.6 tons

TOTAL WASTES 19.8 to 28.4 tons

A.10.5. Control techniques

Straining	+
ECO rinse	+
Static recovery rinse	+
Ion exchangers	+
Electrolysis	+
Recovery rate in copper from the substrate	98 %

Copper salts in solution recovered from ion exchangers or metal copper recovered from electrolysis may be valorized either inside or outside the shop.

A.10.6. Case study : Oxidizing pickling of coils of wire

Pickling bath : H_2SO_4 10 % (weight)
Cu 50 g/l (restored ion electrolysis)
Jet rinse : 3 m3/hr

Cu losses from the substrate :

0.10 % miscellaneous : 0.013 %
rinsing : 0.09 % - metal copper 0.04 %
solved copper 0.05 %
+ 0.15 % recovered Cu on electrolysis.

Provision :

Two oxidizing pickling stations are managed. They are alternatively working and restored on electrolysis. They are added to the standard sulphuric pickling station.

Drag out of metal copper are solved and directly recovered on electrolysis. Electrolysis and straining parameters are optimalized.

Oxidizing bath : H_2SO_4 : 10 % (weight)

H_2O_2 : 100 % : 1.5 %

Jet rinse : 1 m3/hr

Substrate losses : 0.027 % miscellaneous : 0.013 %
rinsing : 0.014 % (solved Cu)
+ 0.28 % recovered Cu 0.18 % standard picklin
0.10 % oxidizing picklin

Copper polluting flow was reduced by 84.3 %.

92.6 % from sulphuric acid were saved (therefore a reduction on saline pollution)

A.10.7. Technical variants

A.10.7.1. Technique preventing or decreasing oxide formation :

THOMSON CSF type continuous casting ; permits decrease in the formation of oxide coating by modification of the metallurgical procédure and by manipulations in reducing medium.

A.10.7.2. Processes other than the standard pickling techniques for reducing wastes and increasing the possibilities of recovery :

1) Helicofil type continuous pickling machine :

Allows for serial pickling with wire-drawing, for example, by shaping the wire like a helix with horizontal axis to perform continuous pickling and to apply static rinses for direct recovery in the pickling bath without causing large increase in waste materials.

2) Oxidizing pickling in H2SO4 + H2O2 medium :

This process is particularly appropriate for the pickling of the oxide layer which is formed over the copper wires between the wire-drawing operations.

The sulphochromic bath is substituted by two successive baths without any intermediary rinse :

- a 10 % volume sulphuric bath producing metallic copper or powdery coppers which adhere to the slug ;
- a 10 % volume sulphuric bath with stabilized hydrogen peroxide which oxidizes the powdery copper into copper sulphate.

Several hydrogen peroxide stabilization processes are marketed.
The dissolved copper may be recovered in a metallic form by electrolysis, whereas with the sulphochromic process, it is discharged in the form of sludge.
Pickling by sulphuric acid - hydrogen peroxide is performed, then, in two baths instead of one for the sulphochromic treatment, but hexavalent chromium and copper wastes are prevented and copper may be recovered in a metallic form by electrolysis. The investment required for making use of electrolysis is quickly compensated by a lower effluent treatment cost and by the valorization of copper.

A.10.7.3. Techniques substituting chemical pickling which result in little or no effluents :

1) Sandblasting :

Projection of abrasives or glass ball in dry or wet medium

2) Emery grinding :

Mainly by polishing strips or metal sheets continuously, makes use of rollers impregnated with abrasives in a wet medium (type 3M)

3) Tribofinishing :

Standard tribofinishing is a mechanical polishing in a wet medium with the possible application of additives.
Tribofinishing has been applied to scour matrix-shaped slugs by the Société Bricart (Bricart Company).
The slugs to be treated are set into motion by vibrations in a torus by an engine with an excentric shaft. The slugs are thus subjected to a double motion :
- rotation over the whole torus
- helicoidal

Friction between the slugs on the one hand, and on plastic abrasives which are more or less loaded on the other hand, result in a controlled wear which is in fact a good finishing treatment.
The process allows the use of nitric acid (case for standard scouring) and chromic acid to be avoided. the wastes are in conformity with the standards in force and are eliminated without preliminary treatment.
Furthermore, this combination of a mechanical control and a chemical control permits the consumption of the copper substrate to be considerably decreased : the copper wastes are in fact 100 times weaker than with the nitric scouring.

A.11. STEEL PICKLING

- Chemical treatment
- Hot or cold bath

A.11.1. Utilization

Steel pickling is used in industry to remove the oxide coat from the surface of the product and to make the surface "clean".

This is the case, for example :

a) After rolling and drawing of the metal sheet or wire, either in a finishing treatment before delivery to the users, or before another surface treatment, such as phosphatation which is used to improve the conditions of lubrication for further processings (drawing)

b) Before finishing surface treatment like :
- Pickling before enamelling
- Pickling before galvanization

Strong acids are added to this pickling, the main ones are : H_2SO_4
HCl

A.11.2. Composition of steel pickling baths

a) Pickling in sulphuric medium :

Hot working at 50° C and in concentrations ranging from 100 to 150 g/l H_2SO_4, the pickling bath reacts on the oxides Fe_2O_3, FeO, Fe_3O_4 and on the iron substrate to form ferrous sulphate (Fe_3SO_4). Etching inhibitors are applied to slow down the attack of iron and to enhance the attack of the oxides. The iron content in the bath is increased. The pickling action is accompanied by a release of hydrogen.

b) Pickling in hydrochloric medium :

Cold working in concentrations ranging from 80 to 120 g/l HCl, the bath reacts on the iron oxides and on the substrate to form ferrous chloride ($FeCl_2$). As in the case of the pickling bath H_2SO_4, the presence of etching inhibitors is necessary. The pickling action is accompanied by a release of hydrogen.

There is an increase in the iron content of the bath.

COMPARISON OF THE TWO PROCEDURES

ADVANTAGES :

H_2SO_4	HCl
- Dissolution by chemical and electrochemical means (considerable release of H_2 which descales. - Large number of concentrated acid moles (32.5 for d = 1.83), hence, relatively low cost. - Easy elimination of $FeSO_4$ by solubility difference between hot working and cold working	- Rapid dissolution of oxides when cold - Nice appearance of slugs after pickling : slugs are light and glossy. - High solubility of $FeCl_2$ in the solution (273 g/l). - Easy application for cold working - Relatively low hydrogen occlusion

DISADVANTAGES :

H_2SO_4	HCl
- Slow pickling velocity when cold hence necessary for hot working. - Pitted appearance of surfaces after pickling. - Weak dissolution of oxides for strong dissolution of iron. - Weak solubility of $FeSO_4$ (70 g/l) - The precipitation of Fe SO_4 on the slugs to be pickled accelerates corrosion. - Strong hydrogen occlusion, hence embrittlement of steels (especially for high resistance steels 150 hbars).	- Weak molar concentration (9.8 moles for d = 1.18) - Little mechanical effect (small hydrogen release) - Cannot be used concentrated and hot (HCl gas release highly toxic).

A.11.3. Location of steel pickling in the technological chains

H_2SO_4 pickling on wire in coils	before galvanization	HCl pickling before enamelling
Prepickling	Acid degreasing	Chemical degreasing Chemical degreasing
Pickling	Pickling	
Hot rinsing	Rinsing	Rinsing
Rinsing	Fluxing	Pickling
	Galvanization	Rinsing
		Neutralization
		Rinsing

The term "rinsing designates the "rinsing function" and implies several tanks.

A.11.4. Simplified substance balance

The wastes generated during the operation of steel pickling are the following :

Drag out wastes :

Drag out in the rinsings of a bath waste having the characteristics of the treatment bath.

Wastes by bath renewal :

This is the restoration of the bath which has a progressive increase in iron, high concentrations of which are detrimental to a good pickling. Additions of acid serve to maintain a pickling activity to a maximum which may be defined by the solubility of ferrous sulphate or of ferrous chloride.

Large pickling plants are equipped with regenerative treatments for pickling baths, whether they are sulphuric or hydrochloric.

In the case of sulphuric acid, a plant like the following one is used :

Cristallization of Fe_2SO_4

Recovery of H_2SO_4 in the circuit ;
and for hydrochloric acid, a plant based on pyro-hydrolysis of iron chloride (LURGI process and RUTNER process) recovering HCl on the one hand, and iron on the other, in the form of iron oxide balls which may be reused.

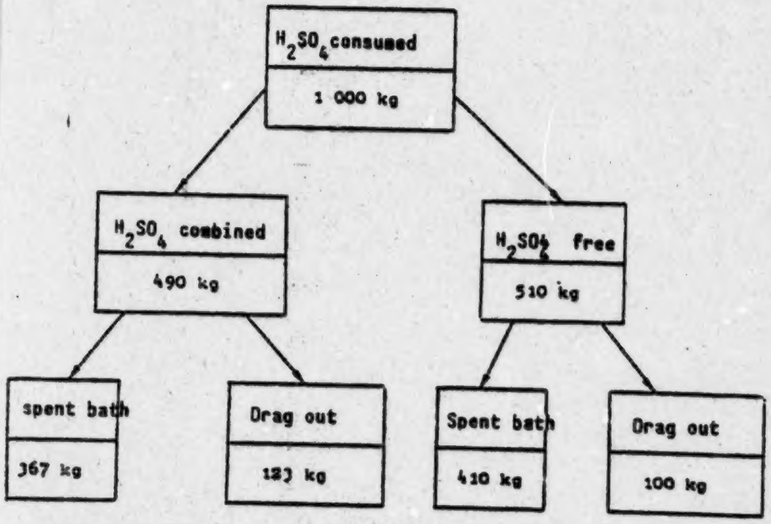
This type of plant is used for productions exceeding 8 to 10 tons/hour of metal which is pickled and placed in ironworks where continuous cold rolling on iron sheets is performed followed by a pickling.

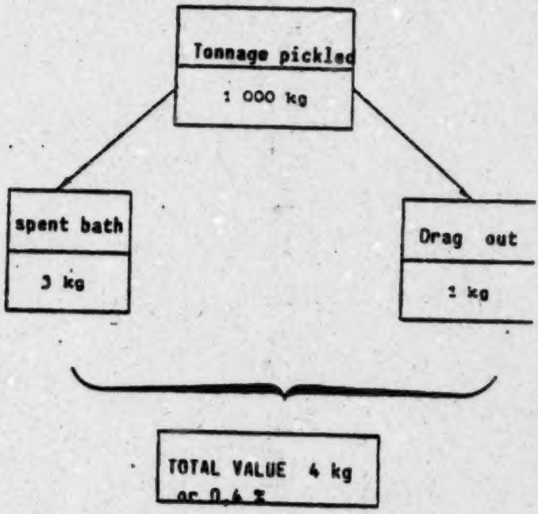
Hydrochloric acid is being more and more used in this type of plant rather than sulphuric acid.

Other recovery processes are available for iron pickling in a hydrochloric medium and for lower production capacities, namely :

1) The recovery of $FeCl_3$ by ion exchangers and bath regeneration

2) Recovery of metallic iron by electro-electrodialysis and HCl bath regeneration.


H_2SO_4 consumed
1 000 kg
H_2SO_4 combined
490 kg
H_2SO_4 free
510 kg
spent bath
367 kg
Drag out
123 kg
Spent bath
410 kg
Drag out
100 kg


Tonnage pickled
1 000 kg
spent bath
3 kg
Drag out
1 kg
TOTAL VALUE 4 kg
or 0.4 %

A.11.5. Technical variants

Mechanical pickling :

Sand blasting granulation : this is the removal of the surface coat of the metal by projection in a dry or wet medium of various kinds of abrasives (sand), granular metal, balls, and of various forms

Brushing : Material is removed by rotary brushing through the use of special emery-coated brushes. This brushing is performed under water. The effluent contains suspended materials which may be filtered.

A.12. LOW OR NON POLLUTING DEPOSIT PROCESS

A.12.1. Precoated metal

For a moderate, or sometimes, substantial, increase in the cost of steel or aluminium per kg or per m2, it is possible to buy in iron and steel or in aluminium industries precoated strips which are either of metal finishing (weldable or not), or of electrolytic Zn. This means that the pollution problems created by the preparation and "in situ" surface treatment are transferred and centralized in about 10 French firms producing precoated metals. As these highly modern lines, which put out metal strips at the velocity of 15 to 100 meters per minute on 0.80 to 1.50 m wide (6000 m2 per hour), are very expensive and highly sophisticated, they invariably have a well designed treatment plant for industrial waste water which meets the most modern specifications using ion exchange water recycling with a continuous automatic control.

As the strip will be shaped after being coated, the metal film or paint deposited must be hard, ductile, flexible and highly adhesive.

The use of this material in the new manufacturing chains or its introduction into standard manufacturing should substantially decrease the pollution flux of the users.

One disadvantage should nevertheless be pointed out : after cutting the sections, this process is applicable to large surfaces and excludes small slugs.

A.12.2. Vacuum evaporation

A.12.2.1. Vacuum pulverization

A.12.2.1.1. : Principle of cathodic pulverization

When a solid is subjected to a bombardment by a beam of ions, it may be observed that above an energy threshold, the surface of this target wears away ; the constituent material of this latter is projected into the surrounding space. When this occurs in a plant having a diode configuration where the cathode is the target, the anode is covered by a layer of cathodic material. This cathodic pulverization is due to a transfer of amount of motion in the first atomic layers of the target. Ions are generally used as projectiles as they are easier to accelerate than atoms ; the energy of these ions is in the range of 300 to 5 000 electron-volts.

The pulverization yield is defined by the number of atoms ejected by an incident ion ; it depends on the energy and the constituency of the latter, on the direction of the trajectory, and finally on the constituency, the crystalline state and the temperature of the target. Argon is the most commonly used gas due to its chemical inertia and because it must weigh less than the atoms to prevent their retrodiffusion, hence, a fall in yield.

The atoms ejected from the target are neutral and are emitted at random in all directions. Their kinetic energy is higher : their velocity is about twice as fast as for evaporated atoms by vacuum heat effect. This partially explains the strong bond of the coatings thus obtained.

Alloys and compounds can be pulverized through this technique by appropriately adjusting the operating conditions. Two variants of this technique make it possible to extend the process for the deposit of compound materials : pulverization under high frequency variable voltage permits insulating materials to be pulverized ; reactive pulverization serves to accomplish the synthesis of compounds from the constituents. In this latter variant, a reactive gas such as oxygen or nitrogen was added to argon. Oxides and nitrides can thus be produced, for example silica from pulverized silicon in oxygen or titanium nitride, TiN, starting with a solid titanium cathode bombarded by nitrogen ions.

The chemical reaction may occur at the surface of the target, on the target-substrate path of the ejected atoms, or at the surface of the substrate. Factors which effect these possibilities are the constituency of the target and the reactive gas, the partial pressure of the reactive gas (average free path) and the target-substrate distance.

A.12.2.1.2. : Techniques of cathodic pulverization

Depending on the constituency of the material to be pulverized and the amount of the deposit to be performed, there are several possible configurations which may be used : diode, triode and magnetron configurations.

The simplest device is the diode or high pressure configuration : two plane electrodes at a distance of several centimeters between which a continuous potential of several kilovolts is applied. The working pressure is about 10^{-2} torr.

In the triode or low pressure configuration, the electrons emitted at the surface of a hot filament are accelerated in the field created by a positive electrode and maintain the load. A magnetic field concentrates the plasma along an axis. A negative voltage is applied to the target placed near the plasma in order to attract the positive ions produced. There is a separation of functions of plasma and pulverization formation.

In the magnetron or high velocity configuration, the anode and cathode are placed on a same perpendicular plane in the direction of pulverization. This permits high deposit velocities to be obtained because of the close proximity of the substrates. The secondary electrons emitted by the target have in this configuration a cycloïdal trajectory and remain right next to the target. The ion attack on the target is then very intense. These characteristics make the magnetron cathodic pulverization technique quite attractive for obtaining thick layers of coatings in a period of time which is comparable to the electroplastic processes. Depending on the objects to be coated, the target can make cylindrical or plane shapes. The process is limited to non magnetic target materials, otherwise the magnetic field is short-circuited.

A.12.2.1.3. Technical impact and development

The operation of this process requires the following provisions :

- a vacuum enclosure, the volume of which is related to the size and type of slugs to be coated ;
- a system capable of producing within the enclosure a pressure limit of 10^{-7} mm of mercury ;
- a system of electrodes permitting electrical connections for a discharge voltage of about 1 KV in the gas used ;
- a system of gas admission into the enclosure, argon is generally used to maintain a determined and constant pressure ;
- an electrical power supply : a few mA for 1 KV ;
- possibly but generally used), a system of automatic control.

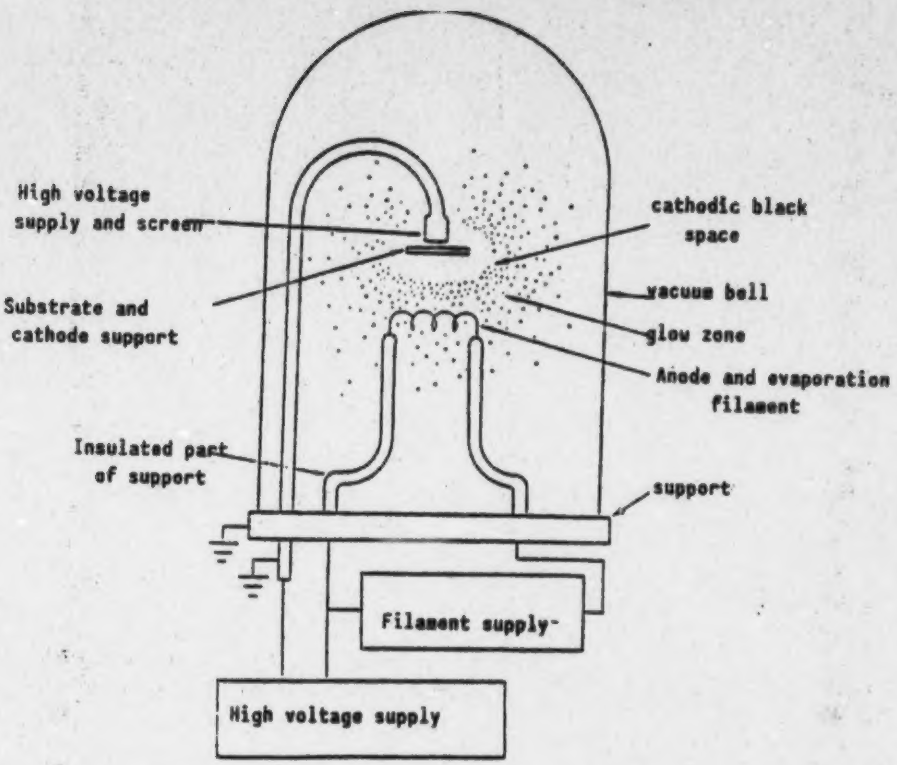
The essential advantage of this process is that it does not create pollution. In fact, it is a vacuum operation and the only effluents produced are solid effluents made up of the deposits applied to the internal parts of the materials used other than the objects to be coated. These internal parts are generally protected from the deposit by thin aluminium sheets which are easy to replace during the periodic cleaning of the deposit facilities. It is without question that the coating operation proper, as usual, must be preceded by an extremely careful surface preparation which constitutesa degreasing, a cleaning and a drying by using the appropriate means : the resulting pollution flux should be insignificant.

A.12.2.2. Ion deposition

A.12.2.2.1. Principles and techniques of ion deposition

Ion deposition consists in ionizing an evaporated metal (or alloy) with the glow discharge of an inert gas. The ions thus created are accelerated by an electric field and deposited on a negative charged substrate.

Generally, argon is used as an inert gas under a pressure of about 10^{-2} to 10^{-3} torr. The voltage applied varies from 500 V to 2 KV.


High voltage supply and screen
cathodic black space
vacuum bell
Substrate and cathode support
glow zone
Anode and evaporation filament
Insulated part of support
support
Filament supply
High voltage supply

In an ionic deposition system like the one shown above, the ionization rate of metal steam does not exceed several per cent. A few improvements must be made to improve this ionization and thus the adhesion :

- multiple hot cathodes, the heat of which free electrons may be placed near the substrate to create an increase in ionization (Multi Hot Cathode I.P.) ;

- an induction coil between the source of evaporation and the substrate stimulates ionization by creating a high frequency magnetic field (R.F.I.P.) ;

- ionic deposition by hollow cathode discharge consists of using electronic bombardment as a source of evaporation from a heated hollow cathode giving a high ionization rate (Hollow Cathode Discharge I.P.) ;

- the ion gun is the process allowing for metal evaporation through heating by induction which causes ionization (I. Gun I.P.) ;

- activated evaporation reactions (A.R.E.) and low pressure plasma deposition (I.P.P.D.) introduces a discharge in addition to the standard evaporation reactions.

The deposition of compounds is obtained by introducing reactive gases (CO_2, N, etc...) in the presence of an evaporated metal in the working chamber.

A.12.2.2.2. Characteristics

The good film adhesion obtained by ionic deposition is explained by the formation of a microscopic alloy layer between the evaporated film and the substrate and by the ionic "pickling" of the slug surface by the shock of argon ions. Ionic cleaning by argon glow discharge is commonly used prior to the standard ionic deposition.

Ionic deposition gives a high density film and a good adhesion as a result of the large amount of energy received by the evaporated molecules caused by their ionization and their acceleration.

Substrates other than metal may be used : a good adhesion is possible on ceramic, glass, plastics. Oxides, nitrides or carbides may be deposited as well as metals.

A.12.2.2.3. Development of vacuum metallization techniques

Ionic deposition and cathodic pulverization are perfectly non polluting processes, as there are no chemicals used in the procedure.

Vacuum metallization is particularly developped in Japan and its uses is growing in the U.S.A. and in Europe.

Ionic deposition is adopted for the objectives of high-priced and demanding industries with respect to coating characteristics which cannot be satisfied by other deposit procedures.

In all cases the investment required is costly, but these processes are non polluting, the deposit velocity is high and the floor space required is smaller than for the standard processes.

Furthermore, these technologies eliminate the need for some treatments before painting.

A.12.2.3. Comparison between the cost-price of a hard chromium coating (electrochemical) and a titanium mono nitride coating (cathodic) pulverization :

We shall attempt to estimate the cost price which should enable us to compare the costs between a hard chromium coating deposit and a titanium nitride coating under similar conditions of application. At the beginning, we are excluding questions concerning constituency and shape of objects to be coated and narrow our estimates to the deposit of one kilo of material.

A.12.2.3.1. Cost price of a hard chromium coating

To evaluate the cost price prior to mark up and taxes, we have used the following formula :

$$PR = S\left[k\ (AH + MO) + To\right].$$

where : AH represents the total amount of kiloampere-hour obtained by dividing the direct production expenditures by the number of kiloameres-hour consumed ;

MO is the total amount of directly productive wages reduced to the actual working hours, i.e. the relation

$$\frac{\text{salaries + expense}}{\text{number of hours}} = \text{hourly value in proportional cost ;}$$

k is a multiplying coefficient which takes into account the fixed or structural expenses. We have taken as value of this coefficient : 1.8 ;

"To" represents the total amount of depreciation and maintenance costs reduced to a unit-value of the production tool, which will be in our case the cubic meter of bath ;

s is a multiplying coefficient which takes into account all expenses not relating to production (costs, fiscal, profit and loss, head office...).

We are going to apply this method of evaluation to the case of a hard chromium plating plant having an average size of 14,000 liters, with 15,000 available amperes operating for one year. With a number of kiloampere-hour consumed of 25,000 kAH, the total values of AH and MO will be respectively 275,000 and 630,000 F, i.e. reduced to KAH ; a cost of 36.20 F, giving with k = 1.8 : 65.16 F. To represents about 20 % of this latter value, i.e. 13.03.

Therefore : k (AH + MO) + To = 78.20 F.

Finally, with s = 1.1 we have 78.20 x 1.1 = 86.01 F per kAH consumed. Accordingly, the hard chromium plating electrogalvanic process requires 23 kAH per kilo of chromium deposited : as a result, the cost price of this latter will be about 1 978 F.

Incidence of depollution :

Compared to the capital investment (land + building + equipment) of 2,000,000 F, the antipollution investment amounts to 400,000 F, i.e. 17 % of the total investment. The operating costs make up about 10 % of the costs. This means that the incidence of antipollution measures in a hard chromium deposit plant of average size (quantity of chromium deposited per year of about one to two tons) is about 15 % of the cost price before taxes and profit. The figures provided are values excluding taxes in 1977 francs and are taken from an ion exchange effluent treatment plant.

In conclusion, the incidence of depollution on the cost price of hard chromium coating is not insignificant. Present legislative taxation measures on effluent disposal are far from being dissuasive in the case where the manufacturer would have at his disposal a waterway with a sufficiently high flow to ensure a dilution in accordance with authorized disposal standards. It is also of economic interest for surface treatment firms to share collectively a common depollution plant.

A.12.2.3.2. Cost price of a titanium nitride coating

To evaluate the cost price of a titanium nitride coating process, we have used the same formula taken for hard chromium. It may be assumed, in fact, that the two production firms have very similar characteristics and that the same calculation criteria may be applied to them. As we have already emphasized, we are limited in the case of TiN to estimates based on a prototype operation and we would like to underline the quite unarbitrary manner in which we have adopted some of the facts.

We have assumed a treatment plant in continuous operation with three stations. I.e. 6,200 hours per year. The deposit speed is 0.5 μm/min. and the aim is to obtain an average thickness of 7.5 μ m over an area of 0.4 m2. The result is a coated area of 1.6 m2/hour with a weight of 63.6 g of TiN.

The annual production will be, then, 394 kg of TiN which is the equivalent to 305 kg of titanium.

With current techniques the yield $\frac{\text{deposited titanium}}{\text{target titanium}} = 0.50$

Therefore, we should begin with 710 kg of target.

The target dimensions are : L = 1 m ; w = 0.4 m and t = 0.025 m, i.e. 1 dm3 of metal or 4.5 kg of titanium.

The number of targets used in one year will be 158. The current cost of a target is about 7,500 F, which brings the metal cost to 1,185,000 F.

Plant cost

We have assumed a plant costing up to 2,000,000 F which with a depreciation in 7 years is the same as an annual depreciation of 285,714 F. The depreciation of building investments has been estimated at 50,000 F, maintenance costs and the costs of replacement parts are estimated at 100,000 F per year.

The cost of electric power is 124,000 F, with the plant having a power of 100 kW ; personnel costs have been evaluated at 600,000 F.

Account was not taken of the plant consumption of cooling water. On the other hand, we have evaluated the requirements for gas, nitrogen and argon in the process. The amount of nitrogen fixed by titanium is 89 kg. The partial pressures respectively of nitrogen and argon in the working enclosure are 6.10^{-4} and 2.10^{-3} torr. In a well designed plant, the amount of nitrogen consumed should not exceed twice the amount fixed on titanium, or 178 kg. As a result, the volume of argon consumed is three times higher than for nitrogen.

Delivered in 10 cubic meter bottles, quality R nitrogen costs 55.2 F per m3 and quality U argon costs 95 F per m3. It may be deduced that the cost of nitrogen will be 7.860 F and the cost of argon will be 40.470 F giving a total of 48.330 F.

By applying the formula adopted above for determining the cost price of hard chromium, we have :

$$PR : 1.1 \left[1,8\ (124,000 + 600,000 + 1.185,000 + 48,330) + (285,714 + 150,000)\right] = 4,354,145\ F$$

for the annual production of 394 kg of TiN.

The cost price per kilo of TiN, before profit and taxes is then 11,051 F, with the assumptions adopted above.

When considering the various factors entering the determination of this cost, it may be observed that the main contribution is from the cost of titanium targets.

The latter could certainly be considerably reduced by adapting the shape of targets to the wear profile ; this would result in a better rate of utilization. The adopting of a manufacturing process making use of a less costly metal could perhaps also be considered.

A.12.2.3.3. Comparison between the cost prices of a hardchromium coating and a titanium mononitride :

To conduct a comparative study, it is necessary to select a specific case of application where titanium mononitride may be substituted for hard chromium. This is a delicate choice to make. In fact, depending on its use, the thickness of a hard chromium coating may vary within a very vast range, from 30µm in the case of slugs working under the effect of sliding + friction, up to 800 to 1 000µm in the case where the slug is subjected to the effect of a high pressure + abrasion and a corrosion.

When considering a serial production as in our preceding calculation, we will select the case of slugs subjected to sliding and friction. We will then compare hard chromium and titanium mononitride coating with respective thicknesses of 30 and 7.5µm. Furthermore, it takes on the average one hour to deposit a chromium thickness of 10µm.The coating surfaces will, then, remain in the electrolysis bath for three hours.

For reasons of comparison, we have adopted the same number of annual working hours both in the case of chromium and for titanium mononitride, i.e. 6,200 hours. This corresponds to a continuous operation of the production chain, hence, to a mass production. It should be pointed out that most chromium (hard) plating shops do piece work, and are therefore often quite considerably overequipped in order to treat a wide range of products, which are used most of the time for very limited series and are not practical for a continuous type of manufacture. Logically, however, we have preferred to compare two types of production under the same conditions.

In taking up again the case of the hard chromium plant examined above, 0.18 kg of chromium will be deposited per hour ; this is for a covered surface of 2.60 m^2 having a thickness of 30µm compared to 4.80 m2 obtained for TiN during the same period. For the estimated cost price per square meter deposited in each case, we have 437 F/m2 for TiN and 427 F/m2 for hard chromium.

With the data adopted, there is no obvious financial advantage to substituting titanium mononitride for hard chromium. It is thus all of the physical and mechanical properties which determine the criterion for selecting TiN coatings, and particularly in the case of slugs which are practical for a mass production, using the plant at full capacity.

ANNEX B

CONTROL TECHNIQUES

B.1. STRAINING

B.1.1. Principle

During the emergence of a slug from an aqueous solution, there is a mechanical drag out of a fine film of liquid containing the elements of the solution. This liquid film becomes diluted in the water of the rinsing or rinsings, depending on the operation. We have then the drag out "q" generating material losses, and thus the pollution flux.

In order to reduce these wastes, the volume dragged out by the emergent surface must first be reduced (raw drag out), then the dragged out liquid should be allowed to flow off.

This objective is reached by straining off the surface above the given solution prior to the transfer into the rinsing or other specific process.

Straining is the operation which consists of eliminating the maximum amount of the solution dragged out mechanically from the emergent surface of a bath. Residual drag out is eliminated during the rinses.

The transfered residual drag out shall be, then, intricately related to :

- the raw drag out at emersion,
- the quality of the straining.

Transferred residual drag out = raw drag out - straining.

The action of the physico-chemical parameters of the galvanoplastic solutions vary with each bath and in different ways.

It may be stated, nevertheless, that in general :

- for a given bath, the residual drag out is proportional to the concentration and to the surface stress, and is inversly proportional to the solution temperature,

- comparison of physico-chemical values of various solutions does not allow the values of drag out from one solution to another to be extrapolated.

Drag out reaches a limit regardless of the straining time required. This limit depends upon the characteristics of the solution and of the slug.

B.1.2. Technical impact

Shape of slugs :

Training programs in design development centres to ensure that the slugs take on "galvanoplastic" shapes so that the drag out limit is minimum and obtained after a short straining.

Position of slugs at emergence :

Training program.

Quality and surface of assemblies :

- training program ;
- careful operation and preventive maintenance of assemblies ;
- careful study of the assemblies.

Bath constituency :

This is a matter of choice which could be determined by one or several standardized measures.

Conditions of emergence :

Control of the emergence velocity and the straining time can only be designed through automatization.

Control of the emergence velocity shall depend on the machine design.

The straining time shall have a technical limit determined by the drying of products entrained at the bath outlet or by the occurence of the surface chemical reaction which is against the desired objectives.

External devices :

Rotation of drums : At the outlet of some chemical baths where the coating formed is not set and is still brittle, the rotation of the drums generates motion among the slugs which in turn damage this coating. The damage caused depends on the slug shape and the bath constituency ;

Blowing : Here again, this technique shall be limited by the possible drying of the slugs which affects the quality of the treatment.

Drying may pe prevented by extrapolating this technique toward water spraying or atomization.

B.2. STATIC RECOVERY RINSE

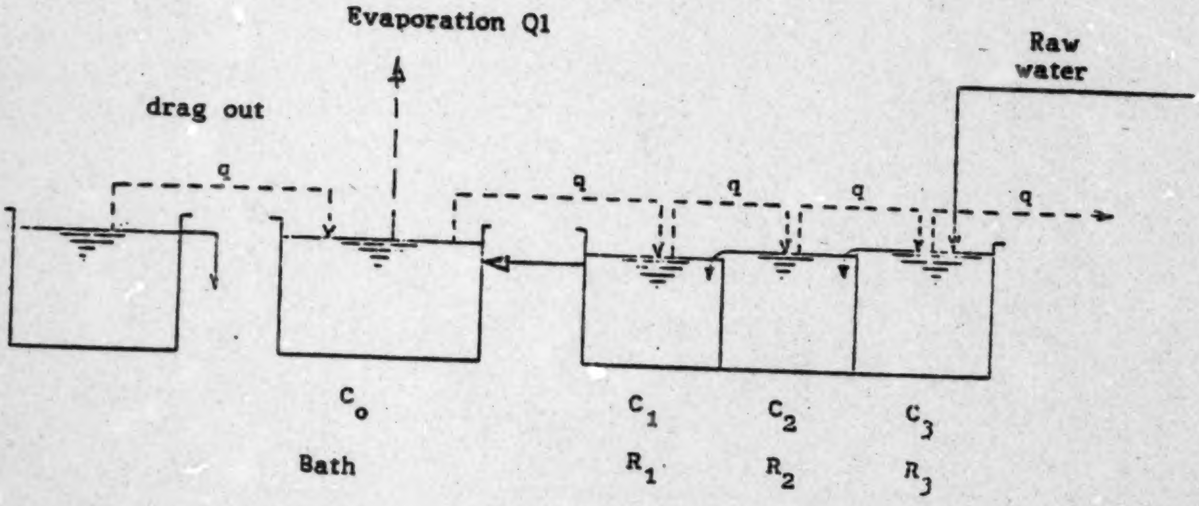
B.2.1. Principle

After a hot-working treatment bath (> 40°), 1 or 2 or 3 static rinses are arranged in a simple cascade to allow for the solution transfer.

Raw water ⟶ 3 ⟶ 2 ⟶ 1 ⟶ bath
or raw water ⟶ 2 ⟶ 1 ⟶ bath
or raw water ⟶ 1 ⟶ bath

The solution coming from 1 serves to compensate volume losses from the treatment bath which are caused either by water evaporation or drag out of blisters from gas release or a combination of the two.

A flow rinse set up after these static rinsings ensure the finish and chemical protection of the following bath :



q = Drag out carried by the treated slugs

B.2.2. Technical impacts

B.2.2.1. Effects of an immersion after treatment in a saline rinse

Rinsing in a liquid containing a diluted quantity of the treatment bath can be detrimental in some cases. Chemical treatments, for example, are performed in the static treatment tank, but in an uncontrolled manner by modifying the desired surface characteristics and thus the final results.

These effects are particularly noticeable during static rinses performed after strong chemical treatments such as :

- satining of aluminium ;
- chromatizing of zamac.

In the case of electrolytic treatments, this technique may result in surface passivation or stains requiring a modification which is easy to achieve in the technological chain. These passivation effects occur, for example :

- after cyanided copper plating when it may be necessary to introduce a depassivation prior to another treatment phase (depassivation often recommended anyway) ;
- after nickel plating when this passivation depends mainly on additional agents (brighteners, penetrants).

In any case, these effects are noticeable when the time of slug transfer or period of time in saline static rinses are excessive, i.e. several minutes.

The study of the technological chain enables a practical solution to this type of disadvantage to be found.

B.2.2.2. Impact of recycling dragged out substances into the bath

B.2.2.2.1.

The recycling of basic products in the treatment bath brings about, of course, a recovery of precious materials, (salts, additives, brighteners). It also entails an even greater recycling and concentration of bath impurities.

Accordingly, the chemical degreasing bath will have a rapid concentration in :

- various suspended materials,
- greases,
- emulsions,
- carbonates.

The cyanided copper plating bath will have a more rapid increase in :

- degradation products of brighteners,
- carbonates resulting from the decomposition of cyanide,
- salts from raw water.

The nickel plating bath will have a more rapid increase in :

- degradation products of brighteners,
- metal impurities (iron, copper, etc...),
- salts from raw water,

The experiment shows :

- that the constituency of the raw water feeding the concentrated baths must be in conformity with the laws of the electroplating technique :
  - avoid waters having a high $TH > 150$,
  - avoid saline waters,
  - perfect solution = demineralized water (non recycled).

- that the concentration increase and impurities of the deposit bath, especially, is compatible with the purification treatments already performed.

- that the treatments are not more frequent than the recycling of drag out.

Impurities are not recycled when they can be eliminated either by standard preventive treatments :

- Filtration with or without activated carbon,
- Continuous selective electrolysis,
- Filtration over exchanger type resin additives, or by curative treatments,
- Oxidation and tank to tank maintenance,
- Precipitation of carbonates and tank to tank maintenance,
- Selective precipitation and filtration.

There is no question that preventive treatments are preferred to curative treatments which generate solution losses, hence effluents. An attempt to ensure careful maintenance of the concentrated baths is necessary and supplementary to the recycling of drag out by static rinse.

It should be pointed out, however, that in some cases, recycling may result in an increase of impurities which cannot be eliminated.

This is the case, for example, of :

- potassium based cyanided baths where CO_3^{--} can be precipitated only by adding calcium ;
- hard chromium plating baths where the constituency of the slugs treated induces the formation of trivalent chromium and the dissolution of iron which entails a dilution and purification on ion exchangers of a new concentration.

B.2.2.2.2.

The recovery of precious products, -metallic salts, various salts, brighteners, various additives, penetrants-, will reduce or eliminate the need for maintenance additions. The nickel bath is a typical case where sulphate and nickel chloride are added and as a result, the operations of dissolution, filtration, and salt reintroduction are eliminated.

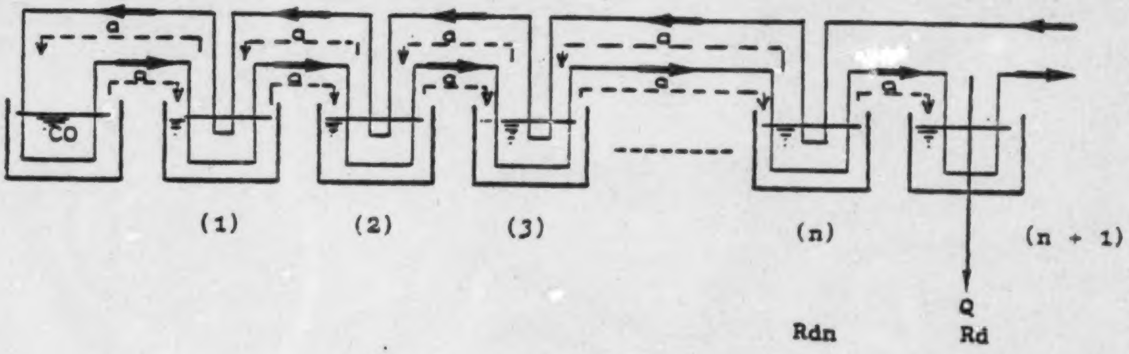
The reintroduction of salts in electrolytic deposit baths will bring about a change in the state of equilibrium of the solution and require a modification to be brought to the anode/cathode ratios by decreasing the anodic surface or by changing the constituency of the anode.

The example here again of the standard nickel plating bath is characteristic, as the anode yield is higher than the cathode yield, there is an increase in the bath concentration with time if all losses are eliminated. In practice, this occurrence is rare, for a small loss of solution during maintenance treatments of the bath compensates the difference in yields.

B.3. ECO RINSE

B.3.1. Principle

ECO rinses are static rinses in which the slugs are immersed before and after the treatment bath without an intermediary flow rinse.



A previous immersion in one or some of the static rinses allows the slugs to reintroduce some of the entrained products, whereas usually the bath volume is supplied by a drag out "Q" containing water originating from the previous rinse. In this technique, the bath is supplied by the same volume Q, which contains then constituent bath products.

Accordingly, there is no modification in the volume summary of the bath under consideration.

This technique shall first be applied to baths which are cold or slightly heated < 40° C.

Slight volume losses of the concentrated bath provoked by small difference in density between the solution entering the bath and the one leaving the bath are compensated mainly by the solution of the ECO rinse.

B.3.2. Technical impacts

B.3.2.1. Effects of the immersion of a substrate in a saline solution before treatment

The immersion of a metal substrate in a saline solution may bring about the corrosion of the latter and hence its dissolution. This effect is possible during the application of the ECO rinse over some substrates and with some baths.

In addition to modifying the surface of the slug and possibly compromising the final treatment, this dissolution will essentially cause an increase in the rate of impurities of the main bath and compromise its efficiency. This will increase the drainage or purification frequency which results in an increase in the volume of effluents.

The ECO rinse will be applied over substrates like steel during electrolytic treatments in a cyanide bath. The rinse will be avoided with respect to application over copper substrates during electrolytic treatments in highly acid or alcaline baths.

In general, the ECO rinse technique will be avoided in the preparation series, with a few exceptions. On the other hand, this technique may be applied for copper, brass and steel pickling in the manufacturing series of semi-finished products :

- steel sheets,
- pipes,
- cylinders,
- etc...

B.3.2.2. Effects of the recycling of products dragged out of the plating bath

See static recovery rinse.

The percentage of recovery obtained by the application of ECO rinses is lower than the one obtained with static recovery rinses. As a result, the possible effects of recycling products will be lower, but will be qualitatively quite comparable.

The effect of the period of immersion in the solution is equally essential and the examination of the technological chain should take this into account (drafting of diagrams and automatism or operation instructions). These queue stations should in no case be neglected before continuing upstream or downstream treatment.

B.3.2.3. Effects of placing and ECO rinse on the structure of the technological chain

This introduction should not present any particular problem in the manual chains where careful operating instructions will ensure its position in the series.

The various designs of modern and automatic galvanoplastic chains cannot be as easily introduced.

In an automatic treatment chain, the physical succession of baths is rarely in the same order as the operational series for the following reasons :

- the desire to have the loading or unloading of the treated slugs at the same place ⟶ manipulation ;
- allows for capacity increases by increasing the main bath at the end of the chain ;
- reduces handling of loads and relative displacements.

B.4. ION EXCHANGE

B.4.1. Principle

The ion exchange resins are synthetic products obtained by polymerization. They form an insoluble solid structure comprising loosely related atoms or groups of atoms, in general H+ cations for cationic resins (RH) ; OH^- anions for anionic exchangers (ROH) and when placed in contact with a liquid containing ions from the solution having the property to exchange, valence for valence, some of their constituent ions (H+ and OH) for other ions found in the solution :

$$RH + C^+ + H2O \rightleftarrows RC + H^+ + H2O$$

$$ROH + A^- + H2O \rightleftarrows RA + OH^- + H2O$$

We shall have a fixation in the direction from left to right and a regeneration process in the direction from right to left.

The ion exchange resins may then fix metals in the solution in three ways :

- as cations on cationic resins
  Iron, Cu, Cr3, Al. ...
- as anionic complex on anionic resins
  Au $(CN)_2^-$, Ag $(CN)_2^-$, $FeCl_4^-$ ...
- as cationic complex
  Cu (NH3)4^{++} ...

The first two possibilities are the most widely used in the industry.

B.4.1.1. Regeneration of solutions by fixation of metal pollutants on ion exchange resins to prevent waste

This involves the fixation of cations in a concentrated acid solution to ensure continuous solution regeneration :

Examples :

- Control of the waste CrO3 by cation fixation :
  - trivalent chromium and aluminium in chromic anode oxidation baths,
  - zinc or cadmium and trivalent chromium in chromic passivation baths,
  - iron, zinc, copper in the static rinses of hard chromium plating ;
- Control of phosphoric acid waste by fixation of iron cation :
- Control of hydrochloric acid waste by fixation of the anionic complex $FeCl_4^-$

B.4.1.2. Recycling of drag out loss by fixation and concentration on ion exchange resins

A determined part of the drag out loss is fixed on the cationic or anionic resins in closed or open circuit which may be :

- cations like copper,
- anions like 6 chromium anion,
- copper or silver anionic complexes ;

– Control of copper wastes in the rinse stations of :

- copper acid,
- copper pickling

by copper fixation and reintroduction of the elutriates into the bath under consideration.

– Control of CrO3 wastes in the rinses of the chromium plating station by Cr6 fixation and reintroduction of the result into the bath under consideration.

B.4.2. Evaluation of reducing the pollution flux

The decrease in pollution flux may be estimated case by case, but it is difficult to define a general rule. Nevertheless, the main characteristic parameters shall be as follows :

B.4.2.1. For the first case : solution regeneration

Solution purification of ion exchangers shall then be proportional to :

a) the bath volume ;

b) the bath composition ;

c) the bath frequency.

In practice, considerable differences may be observed in the breakdown of waste products, depending on the nature of each production, i.e. :

- drag out losses,
- degradation wastes,
- drainage wastes.

Taken into account that degradation wastes are constant per surface unit, the other wastes vary in opposite directions :

drainage wastes decrease when entrainment wastes increase (auto-purification and product readjustment) and inversely.

Knowledge of the input-output balance and a control over drag out shall be of primary importance (see straining).

B.4.2.2. For the second case : recycling into the plating bath of the dragged out waste

Fixation of the pollutant will include all of the waste in the drag out. This pollutant flux will be restored in the form of regeneration eluates, the volume of which will depend on :

- the fixation process and direct or indirect restoration ;
- whether all or part of the regenerated eluate is taken into account ;
- the regeneration process : outside regenerant or not.

It may be considered that the restoration shall exceed 80 % of the material considered in a volume which varies with the nature of the problem and the technique used.

Standard techniques of applying ion exchangers result in semi-concentrated eluates ; it is often necessary to ensure an additional concentration to decrease the volume restored and allow for its reintroduction.

Accordingly, the ion exchange shall be one link in the control chain coordinated with supplementary techniques.

B.4.3. Technical impacts

B.4.3.1. Regeneration of solutions

B.4.3.1.1. Effect of stabilizing the active solution

Stabilization of the solution concentration under consideration shall have positive effects on the surface treatment process, namely :

- constancy of the solution activity,
- constancy of the treatment period,
- constancy in the quality of the finished products.

B.4.3.1.2. Secondary effects brought about by purification

These effects must be considered when the solution composition is not completely known. In this case, the fixation of elements, other than those to be eliminated, to regenerate the solution may bring about an unbalance in the treatment bath activity and jeopardize its efficiency.

B.4.3.2. Recycling of the drag out losses

Effects brought about by the recycling of a solution in the treatment bath :

These effects shall depend mainly on the process and the bath under consideration.

Cationic or anionic fixation of a given element may accompany the fixation of secondary elements which shall become concentrated in the bath.

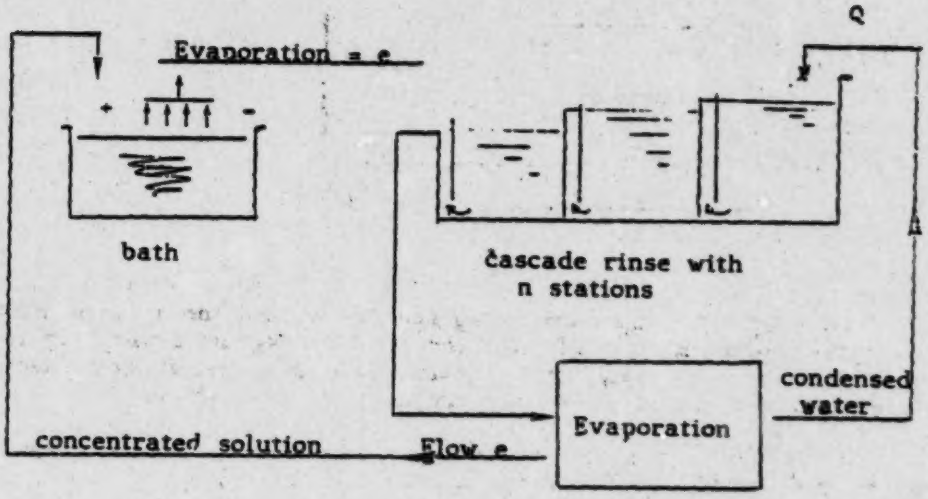
Those effects shall not be very different from those already described in the technique of static recovery rinses :

- water constituency ;
- continuous purifications ;
- etc...

B.5. EVAPORATION

B.5.1. Principle

Theoretically, this process permits the elimination of drag out wastes exiting a hot bath and allows for working in a closed circuit Water + Products.


Q
Evaporation = e
+
-
bath
cascade rinse with n stations
condensed water
Evaporation
concentrated solution
Flow e

All of the product wastes are recycled :

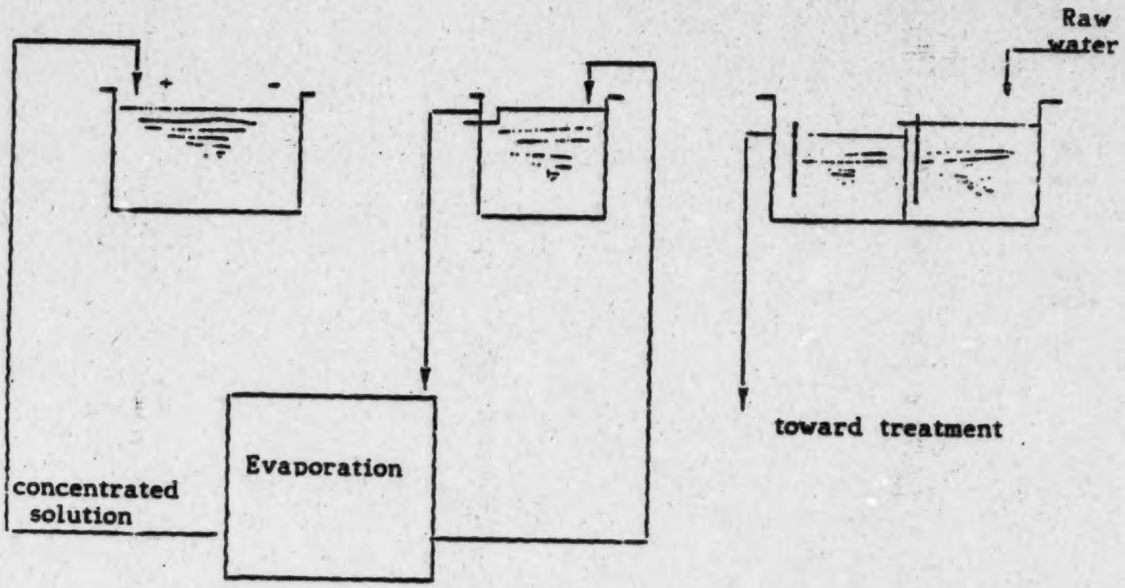
- product additions are reintroduced into the bath after concentration by evaporation ;
- evaporated, then condensed rinse water supplies the cascade rinse.

The three parameters :

- bath evaporation,
- drag out,
- pereentage of products to be recovered,

which condition the application and size of the process.

Product recycling can be complete. This is the case of the diagram depicted above where there is the recovery of all or part of the drag out wastes and in this case, part of the wastes are subjected to another treatment.



In the same operating conditions and for a same dilution ratio in the third cascade station, the second diagram could recycle 80 to 95 % of the wastes with considerably lower evaporation and operating costs than to recycle 100 % of the products by diagram 1.

In both cases, the number of rinses set up is to be estimated in the general study of the item.

B.5.2. Evaluation of the flux reduction

B.5.2.1. Total recycling

As we have seen, the evaporation procedure results in the recycling of the entire loss in products :

- product additions,
- water.

The pollution flux reduction will be very close to 100 %, account taken of the various wastes from cleaning or from circuit draining.

B.5.2.2. Partial recycling

In this case, the pollution flux reduction shall be decided and shall depend on the evaporated rinse concentration and hence on the dilution ratio of this station.

The recovery percentage selected shall be determined :

- from the dilution ration
- from the rinse flows
- from the evaporator capacity.

B.5.3. Technical impact

B.5.3.1. Temperature effects on bath constituency

Some organic components of galvanoplastic baths may be degraded at the temperature of water evaporation. This shall bring about :

. an artificial consumption of additives,

. a hazardous concentration of degradation products in the treatment bath.

As a result, the main solution evaporation processes of galvanoplastic baths require, partially due to the reasons depicted above, vacuum evaporation.

B.5.3.2. Effects of recycling dragged out substances in the bath

This recycling is identical to the recycling brought about by static recovery rinses. The effects shall be similar.

B.5.3.2.1.

The recycling of basic products in the treatment bath brings about, of course, a recovery of precious substances (salts, additives, brighteners). It also causes the recycling and concentration of even larger quantities of bath impurities.

The experiment shows :

- that the concentration of impurities, particularly in the case of deposit baths, is compatible with the purification treatments already performed ;

- that treatments are not more frequent than drag out recycling.

No impurities are reintroduced which cannot be eliminated :

- Either by standard preventive treatments :
  - filtration with or without activated carbon,
  - continuous selective electrolysis,
  - filtration an additives, exchanger type resins.
- Or by curative treatments :
  - Oxidation and tank to tank maintenance,
  - precipitation of carbonates and tank to tank maintenance,
  - selective precipitation and filtration.

It is obvious that preventive treatments will be preferred to curative treatments which generate solution losses, hence, effluents. Careful bath maintenance is a necessary and complementary requirement to the recycling of drag out.

Let us take note, however, that -in some cases- the recycling may be combined with a solution purification procedure before reintroduction into the main bath.

Example :

- Purification of a chromic solution on iron exchangers before evaporation and reintroduction.

B.5.3.2.2. The recovery of precious products

metal salts,
various salts,
brighteners,
various additives,
penetrants

will reduce or eliminate the need for additions during maintenance procedures. The nickel bath is a typical case where the additions of sulphate and nickel chloride are eliminated and thus the procedures of dissolution, filtration and salt reintroduction are eliminated.

The reintroduction of salts into electrolytic deposit baths will modify the solution equilibrium thereby requiring the modification of the anode/cathode ratios by decreasing the anode surface or changing the anode constituency.

The example of the standard nickel plating bath, once again is characteristic. Since the anode yield is higher than the cathode yield, account taken that all wastes are eliminated, an increase in the bath concentration may be observed over time. In practice, this occurrence is rare, since the moderate loss of solution during maintenance treatments compensates the difference in yields.

EFFECTS OF RECYCLING CONDENSATED WATER (total recycling)

The recycling of condensated water containing some ppm of salinity will improve the quality of the slug finishing rinse. In the case of chromium plating, for example, the stains caused by possible water hardness will be avoided and the finishing costs eliminated.

B.6. REVERSE OSMOSIS

B.6.1. Principle

If a semi-permeable membrane and pure water are placed in an aqueous solution, the water will pass through the membrane to dilute the solution ; the equilibrium will occur when the pressure exerted by the highest level of solution shall be equal to the osmotic pressure : this is the phenomenon of osmosis.

Inversely, if a pressure higher than the osmotic pressure is exerted on the aqueous solution, the opposite effect occurs, i.e. the aqueous solution becomes concentrated as pure water passes through the membrane and into the next area.

By introducing polluted waters into the area containing continuous aqueous solution under increased pressure, the effect will be a continuous passage of pure water into the area containing the pure water and a continuous overflow of the more concentrated aqueous solution.

The pure water translation velocity through the membrane is given by the formula :

$$v = K\ f.\ \frac{(\Delta P - p)}{d}$$

v = translation velocity

K = constant of proportionality

ΔP = pressure difference between two sides of the membrane

d = membrane thickness

f = membrane surface

In order to obtain a high translation velocity, the membrane must be as thin as possible. As it must also be resistant to a high pressure, up to 40 Atm, a support layer is glued to it - the bond of several membranes comprises one unit or "modulus".

Reverse osmosis shall be use for excessive salinity when ion exchangers cannot be used.

B.6.2. Technical impact

This technique is generally coupled with a cascade rinse to minimize the water volume.

This procedure used in closed circuit permits the recycling in the treatment bath of more than 95 % of the chemical products contained in the rinse waters.

It is not useful to supply the circuit with water, except to compensate losses by evaporation. Chemical agents are not added to the bath except to make up for those consumed by deposit.

The structure and life of the membrane determine the success of applying this technique.

The use of a filter upstream from the membrane prevents the latter from becoming plugged by solid particles.

The concentration of impurities in this closed circuit can be corrected by using ion exchange, chemical precipitation or activated carbon.

The obstacles to using reverse osmosis are : pH variations (especially outside the range 2.5 - 11), and the presence of oxidants.

The application of membranes made of cellulose acetate and of polyamide permits reverse osmosis to be recommended for the following cases (within the boundaries defined) :

- watts (nickel)	with permeable membranes in boric acid
- nickel sulphamate	with permeable membranes in boric acid
- nickel fluoroborate	with permeable membranes in boric acid
- copper pyrophosphate	with possible decomposition of pyrophosphate
- zinc chloride	with evaporation in closed circuit
- copper cyanide	with low pH
- zinc cyanide	with low pH and an evaporation in closed circuit
- cadmium cyanide	with low pH and an evaporation in closed circuit

and is not recommended in the following cases :

- chromic acid (membrane destruction)
- cyanided baths with very high pH (membrane destruction)

B.7. ELECTROLYSIS

B.7.1. Principle

During the electrolysis of a solution containing metallic salts, the separation of metals takes place at the cathode, and various electro-chemical reactions take place at the anode.

In order that reactions such as metal separation on the cathode may take place, a given voltage : the breaking down voltage must be applied to the electrodes ;

The occurrence of cathodic overvoltage and particularly of anodic overvoltage produces secondary reactions and effect metal separation yields at the cathode.

The quality of the deposit obtained during the recovery at the cathode is of little importance. On the other hand, it is preferable to deposit the greatest amount of metal in a given time interval to have the smallest possible electrolysis cell. Theoretically, the increase of electrolysis current should bring this about, but in general, this increase cause hazardous secondary reactions at the recovery thereby generating a limited current density. Inversely, the metallic concentration cannot reach 0, since the limited current density becomes too low and the deposit velocity too slow.

The recovery of metals by standard electrolysis shall be accomplished, then, by circulating the treatment bath over an electrolysis cell, the anodes of which shall be made of a material which is insoluble in the anodic phase in the environment under consideration, for example : lead, graphite, titane, iron. The electrodes will be :

either flat and parallel

or circular and parallel.

The size and design of the recovery cells must take into account the following parameters :

- amount of metal to recover in the time unit,
- densities of current limit,
- possible operating time,
- constituency of deposit compared to environment,
- secondary reactions at electrodes,
- metal reuse.

B.7.2. Evaluation of the flux reduction

Whether the electrolysis bath is a static rinse or non ferrous metal pickling bath, it will become stabilized in metal in solution with a concentration C_E which will depend on the parameters previously described.

The pollution flux in the rinse(s) which follow(s) will be proportional to this concentration and characteristic of the dilution ratio $\frac{Co}{CE}$.

NOTE : The various volume losses of the metallic deposit bath shall be made up by priority by the solution of the electrolysis bath, provided that the electrolysis solution is compatible with the bath (degradation products from the electrolysis).

B.7.3. Technical impact

B.7.3.1. Effect of the immersion of a substrate in a saline solution after electrolytic treatment

During the electrolysis of a static rinse following an electrolytic deposit bath, the substrate will be immersed in a solution containing :

a) basic electrolysis diminishing the concentration in metal,

b) electrolysis decomposition products, in general, oxidation products.

We are in the same situation again as during the previous studies : ECO rinse or static recovery rinse with the same requirements, particularly regarding the period of immersion in this type of bath which must not be too long.

B.7.3.2. Effect of the metal recovery

The metal recovery in the form of an electrode will lead to the following various possibilities :

B.7.3.2.1. Waste control

. Reinsertion of the recovered metal as anode into the deposit bath. This will be possible when the deposit has the desired constituency : the conditions of electrolysis will bring about a deposit of good quality in the form of a plate, for example (copper, tin, silver, etc...)

. Regeneration of the bath activity by metal separation. Example : electrolysis of the copper pickling bath in an H2SO4 medium results in the control of sulphuric acid wastes (regeneration of the activity) and in the valorization of the pickled copper.

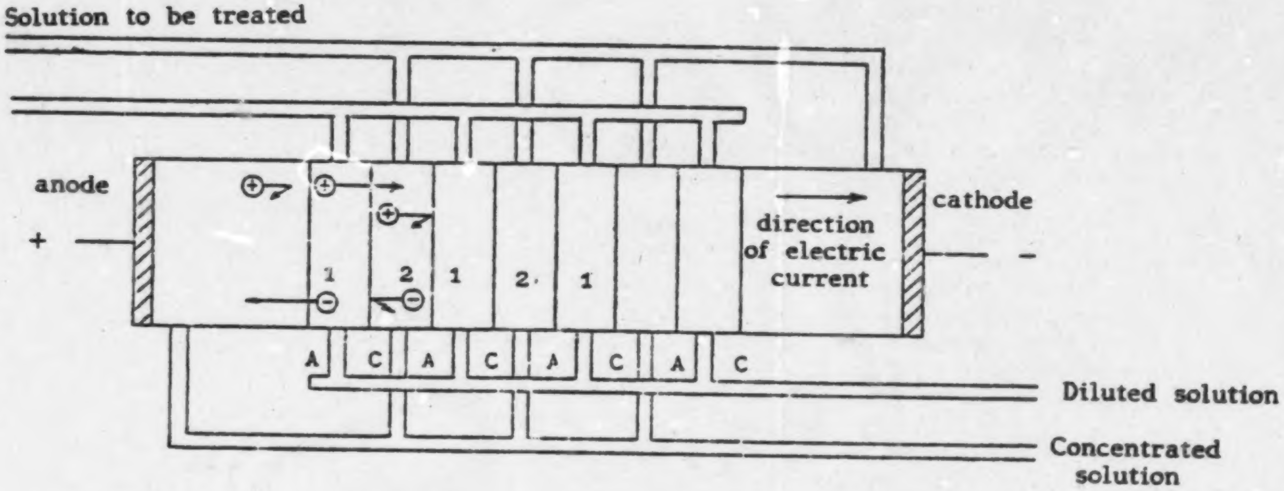
B.7.3.2.2. Valorization

This is the reinsertion of the recovered product into the outside circuits for retransformation :

- copper from copper pickling
- silver in the form of powder
- gold for refining
- etc...

B.8. ELECTRODIALYSIS

B.8.1. Principle


Solution to be treated
anode
+
cathode
−
direction of electric current
1
2
1
2
1
A
C
A
C
A
C
A
C
Diluted solution
Concentrated solution

A : anionic membranes

C : cationic membranes

Electrodialysis uses semi-permeable membrane properties, osmotic effects related to the effects of electrolytic ion migration and ion-exhange membrane properties.

The diagram above depicts the operating principle of an electrodialyser. The compartments are separated alternately by anionic membranes through which only anions can pass through, and by cationic membranes through which cations can pass through.

Under the effect of the electric current applied to the electrodes, the cations migrate from compartment 1 to Compartment 2 by passing through a cationic membrane and are stopped by an anionic membrane.

Inversely, the anions migrate in the opposite direction, exiting compartment 1 through the anionic membrane and are stopped by the cationic membrane.

Consequently, compartment 1 looses salts and compartment 2 increases in salts (salts ionized in the solution).

Electrodialysis permits then :

- some ions to be separated from a solution,
- a solution to become concentrated.

In practice, electrodialysis will be applied in two manners :

In ion separation, there is the purification of the solution containing undesirable cations. This is the case of chromic solutions containing iron, copper, zinc, trivalent chromium, etc... Cations are concentrated in the anionic compartment where the reoxidation of trivalent chromium into hexavalent chromium also occurs.

Depending on the use of cells and membranes, there may be a concentration of chromic solution or of impureties. This is the case of the static rinse treatment following chromium plating where there is a concentration and purification of hexavalent chromium (concentration compartment) whereas the solution of the static rinses diminishes or becomes stabilized (dilution compartment).

This separation by electrodialysis is also applied for the continuous regeneration of hydrochloric pickling baths for steel where iron is separated as a metal and hydrochloric acid is restored.

With respect to concentrating a solution, electrodialysis is used to concentrate chromic acid exiting a static rinse up to concentrations of 200 to 300 g/l CrO_3. This solution is used to compensate volume losses of chromium plating baths.

In other applications and depending on the types of baths, there is a direct transfer from the rinse to the concentrated bath without a transfer of volume.

B.8.2. Reduction of the pollution flux - evaluation

The two cases of applying this technique should be examined :

B.8.2.1. Separation

This is the continuous regeneration of baths which prevent their drainage and the detoxication of their components. The same effects occur here as for the purification of baths using ion exchangers to prevent losses (acid, CrO_3, etc...) The effects differ with respect to the products extracted. It appears that they can be more easily valorized with electrodialysis than with ion exchangers.

The reduction of the pollution flux is the elimination of bath drainage and its effects.

The following will be taken into consideration :

- bath volume
- bath composition
- drainage frequency

(see ion exchangers)

B.8.2.2. Concentration

A comparison should be made of the static rinses, ECO rinses, electrolysis techniques with respect to the drainage of the flux reduction. The concentration of a static rinse by electrodialysis is limited to a few grams per liter of toxic or salinity.

The decrease in pollution flux varies to the extent where the concentrated volume obtained may be reintroduced into the bath under consideration. This problem does not apply in the case of a direct transfer.

B.8.3. Technical impact

B.8.3.1. Effects of immersing a substrate in a saline solution after electrolytic treatment

Refer to :

- Static recovery rinse
- ECO rinse
- Electrolysed rinsing

B.8.3.2. Effects of stabilizing the solution concentration

- Stabilization of the solution activity
- Stabilization of the treatment period
- Stabilization of the quality of the finished product.

B.8.3.3. Effects of reintroducing a solution into the treatment bath

As in the case for separation by ion exchangers, these effects depend on the process and the bath.

The properties of electrolysis apply to ionized elements, and multiple baths of the metal finishing industry utilize non ionized bodies, the migration of which is unknown in the electrodialyser. Consequently, depending on the constituency of the solution treated, some transfers do not occur or occur incompletely. These effects could bring about an unbalanced solution which should be remedied or an increase in concentration of a type of element that should be discharged.

B.8.3.4. Effects of the recovery of products as a metal

This is a secondary effect of the pickling bath regeneration where the metal recovery in metallic form will enhance its valorization.

ANNEX B - APPENDIX 1

……

COST PRICES OF CONTROL TECHNIQUES

From :

"Development document for proposed existing source pretreatment standards for the electroplating point source category".

E.P.A. - February 1978

(a dollar base of January 1976 was used for all costs)

Other quotations about cost prices of effluent treatment techniques are brought up in Appendix 2 to Annex C.

In general, the tables show costs for investment, total annual cost, depreciation, cost for capital, operation and maintenance (less energy and power), and energy and power. These costs are defined under the subheadings to follow. Not all of these costs pertain to all technologies. Energy costs are often negligible, and some techniques such as rinsing have no maintenance costs beyond what is already required for the plating line.

INVESTMENT

Investment is the capital expenditure required to bring the technology into operation. If the installation is a package contract, the investment is the purchase price of the installed equipment. Otherwise, it includes the equipment cost, cost of freight, insurance and taxes, and installation costs.

TCTAL ANNUAL COST

Depreciation

Depreciation is an allowance, based on tax regulations, for the recovery of fixed capital from an investment to be considered as a noncash annual expense. It may be regarded as the decline in value of a capital asset due to wear and obsolescence.

Capital

The annual cost of capital is the cost, to the plant, of obtaining capital, expressed as an interest rate. It is equal to the capital recovery cost (see the following section on cost factors) less depreciation.

Operation and maintenance

Operation and maintenance cost is the annual cost of running the wastewater treatment or rinse equipment. It includes labor and materials such as waste treatment chemicals. As presented on the tables, operation and maintenance cost does not include energy (power or fuel) costs because these costs are shown separately.

Energy and power

The annual cost of power and fuel is shown separately, although it is commonly included as part of operation and maintenance cost. Energy and power cost has been shown separately because of its importance to the nation's economy.

TECHNOLOGY COSTS AND ASSUMPTIONS

Specific cost data were generalized to obtain the cost correlations by means of certain assumptions. Correlations were then verified by checking them against independant sets of cost data. The specific assumptions for each wastewater treatment process and rinse technique are listed under the subheadings to follow. Costs are presented as a function of process influent water flow rate except where noted differently in the process assumptions. For all rinse techniques, a programmed hoist operation was assumed, and line conversion costs were included. For operations of the cycle elevator conveyor type, line conversion costs to incorporate rinse techniques are approximately 10 times the conversion cost of programmed hoist operations.

SINGLE STAGE RUNNING RINSE

The costs of single stage running rinses are discussed below. Costing assumptions are :

A. Unit cost is based on one open top stainless steel tank with a depth of 1.22 meters (4 feet), length of 1.22 meters (4 feet), and width of 0.91 meters (3 feet). Investment cost includes all water and air piping, a blower for agitation, and conversion costs for programmed hoist operation.

B. Operation and maintenance costs include an electrical charge for the blowers based on a capacity of 1,219 liters/min/sq. meter of tank surface area (4 cfm/sq ft) at a discharge pressure of 1,538 kg/sq. meter of tank depth (1 psi/18 in.), Fan efficiency is assumed to be 60 per cent. A rinse water charge is also included. Rinse maintenance charges are assumed to be negligible when compared to normal plating line maintenance and are ignored.

For a dragging flow rate (i.e., plating tank drag out flow rate) of 22 liters/hour and a rinse ratio (plating solution concentration/final rinse effluent concentration) of 363, the following typical costs are incurred :

Investment ($)	3,505
Cost of capital ($/year)	224
Depreciation ($/year)	701
Operation and maintenance (less energy and power) ($/year)	2,156
Energy and power ($/year)	126
TOTAL ANNUAL COST ($/year).....	3,206

COUNTERCURRENT RINSE

The costs of countercurrent rinsing without using the first stage for evaporative loss recovery are presented as a function of the number of rinse tanks utilized. Costing assumptions are :

A. Unit cost is based on open top stainless steel tanks with a depth of 1.22 meters (4 feet), length of 1.22 meters (4 feet), and width of 0.91 meters (3 feet). Investment cost includes all water and air piping, a blower on each rinse tank for agitation, and programmed hoist line conversions.

B. Operation and maintenace costs include a cost for electricity for the blowers based on a capacity of 1,219 liters/min./sq. meter of tank surface area (4 cfm/sq. ft.) at a discharge pressure of 1,530 kg/sq. meter/meter of tank depth (1 psi/18 in.). Fan efficiency is assumed to be 60 per cent. A water charge based on a rinse ratio of 8,180 is also included. Rinse maintenance charges are assumed to be negligible when compared to normal plating line maintenance and are ignored.

Number of Rinse Tanks	3	4	5
Investment ($)	8,203	10,553	12,902
Annual costs :			
capital cost	523	673	823
Depreciation	1,641	2,111	2,580
Operation and maintenace costs (excluding energy and power costs)	20	9	6
Energy and power costs	377	503	628
TOTAL ANNUAL COSTS ($)............	2,561	3,296	4,038

RENT RINSE USED FOR RECOVERY OF EVAPORATIVE PLATING LOSS

The costs of countercurrent rinsing with a rinse flow it to replace plating tank evaporative losses are presented. ire tabulated for various evaporative rates which are equal water flow rates. Costing assumptions are :

Unit cost is based on a sufficient number of rinse stages to replace the evaporative loss from a plating bath at approximately 60 degrees C while also maintaining a rinse ratio of 8,180.

Investment costs include open top stainless steel tanks with a depth of 0.91 meters (3 feet), length of 1.22 meters (4 feet), and width of 1.22 meters (4 feet). All water and air piping, a blower on each rinse tank for agitation, a liquid level controller, solenoid, and pump are also included in the investment cost. Operation is assumed to be programmed hoist and line conversion costs are included.

Operation and maintenance costs include a cost for electricity for the blowers based on a capacity of 1,219 liters/min/sq. meter of tank surface area (4 cfm/sq. ft.) at a discharge pressure of 1,538 kg/sq. meter/meter of tank depth (1 psi/18 in.). A fan efficiency of 60 per cent is assumed. A water charge is also included. Rinse maintenance charges are assumed to be negligible when compared to normal plating line maintenance and are ignored.

rate			
	15.3	24.0	50.8
($)	13.753	11,352	8.951
:			
osts	877	724	571
ion	2,751	2,270	1,790
and maintenance cluding energy r costs)	4	6	14
nd power costs	628	503	377
L COST ($)	4,261	3,504	2,752

Savings due to recovery of plating solution are not presented in this table.

SPRAY RINSE

The costs of spray rinsing with a rinse flow rate sufficient to replace plating tank evaporative losses are presented as a function of the plating tank evaporative loss which is equal to the rinse water flow rate. Costing assumptions are :

A. Unit cost is based on one open top stainless steel tank with a depth of 0.91 meters (3 feet), length of 1.22 meters (4 feet), and width of 1.22 meters (4 feet) with 6 sray nozzles, conductivity meter controller, pump, solenoid, piping, and conversion of programmed hoist operation.

B. Operation and maintenance cost is the rinse water charge based on replacing the plating tank evaporative losses. A combined spray efficiency of 50 per cent is assumed. The combined spray efficiency accounts for the amount of spray water hitting the part and the amount of the part that can be hit by the spray. Power, filter replacement, and maintenance costs are negligible when compared to normal plating line operation and maintenance and are ignored.

Evaporative Rate (liters/hr)	60.8	101.3	135.0
Investment ($)	3.472	3.472	3.472
Annual costs :			
Capital costs	221	221	221
Depreciation	694	694	694
Operation and maintenance costs (excluding energy and power costs)	16	27	36
Energy and power costs	0	0	0
TOTAL ANNUAL COST ($)	932	943	952

Note : Savings due to recovery of plating solution are not presented in this table.

STILL RINSE

The costs of still rinsing with a return from the rinse tank sufficient to replace plating tank evaporative losses are presented as a function of the plating tank evaporative rate. Costing assumptions are :

A. Unit cost is based on one open top stainless steel tank with a depth of 0.91 meters (3 feet), length of 1.07 meters (3.5 feet), and width of 1.07 meters (3.5 feet) with 1.041 liter capacity. Investment cost includes the tank, liquid level controller, pump, and conversion of programmed hoist operation.

B. The operation and maintenance cost is the rinse water charge based on replacing the plating tank evaporative losses and maintaining the effluent rinse concentration less than or equal to 30 per cent of the influent concentration (i.e. plating tank drag out). The still rinse tank is assumed to be hose filled and dumped to the plating tank. Maintenance and power costs are negligible when compared to normal plating line maintenance and power costs and are ignored.

Evaporative Rate (liters/hr)	29.7	59.5	99.1
Investment ($)	2,971	2,971	2,971
Annual costs			
capital costs	190	190	190
depreciation	594	594	594
Operation and maintenance costs (excluding energy and power costs)	8	16	27
Energy and power costs	0	0	0
TOTAL ANNUAL COSTS ($).............	792	800	810

Note : Savings due to recovery of plating solution are not presented in this table.

ION EXCHANGE - IN-PLANT REGENERATION

Ion exchange costs with in-plant regeneration are presented. Costing assumptions are :

A. The unit size is based on two columns to allow both cation and anion exchangers of sodium and chloride, rather than hydrogen. An average resin life of seven years is assumed.

B. Regeneration is performed with a 10 per cent aqueous solution of sulphuric acid. 2.0 kg of sulphuric acid are required for each 1.0 kg of removed contaminants. Regeneration requirements are based on typical influent values for chromium, cadmium, and nickel.

C. Heavy metals removal is assumed to be complete.

Flow rate (liters/hr)	95	4,731	9,463
Investment ($)	2,789	27,558	42,660
Annual costs :			
capital costs	178	1,758	2,722
depreciation	558	5,512	8,532
operation and maintenance costs (excluding energy and power costs)	951	9,338	15,912
energy and power costs	0	0	0
TOTAL ANNUAL COST ($)............	1,687	16,608	27,166

ION EXCHANGE - SERVICE REGENERATION

Ion exchange costs with service regeneration are presented. Costing assumptions are :

A. Unit sizes and pump power requirements are based on data supplied by the manufacturer for standard system flow capacities.

B. Replacement units are installed in place of exhausted units every two months. Regeneration is performed by the manufacturer for a service charge.

C. Metals, cyanide, and sulfates are removed to levels specified by the manufacturer.

Flow rate (liters/Hr)	795	4,731	9,463
Investment ($)	5,040	16,372	21,840
Annual costs :			
capital costs	345	1,044	1,393
depreciation	1,080	3,274	4,368
operation and maintenance costs (excluding energy and power costs)	1,737	6,241	10,250
energy and power costs	68	203	406
TOTAL ANNUAL COST ($)..............	3,230	10,762	16,425

CYCLIC ION EXCHANGE

The costs for cyclic ion exchange are presented as a function of influent chromium mass. The same costs can be generated with nickel as the critical influent mass if the following mass equivalents are maintained :

Chromium mass (kg/hour)	Nickel mass (kg/hour)
0.91	3.40
2.72	7.47
4.08	9.98

Costing assumtions are :

A. Unit cost is determined by the influent chromium or nickel mass. Investment cost includes the skid mounted ion exchange system and start-up servicing. An auxiliary evaporator is not generally recommended by the manufacturer, and costs for this device are not included.

B. Operation, maintenance, and utility costs are included. The utility cost is an electrical charge for pump operation.

Influent chromium mass (kg/hr)	0.91	2.72	4.08
Investment ($)	13,695	27,034	34,748
Annual costs :			
Capital costs	874	1,725	2,217
Depreciation	2,739	5,407	6,950
Operation and maintenance costs (excluding energy and power costs)	2,690	8,278	12,503
Energy and power costs	203	401	515
TOTAL ANNUAL COST ($).................	6,506	15,811	22,185

REVERSE OSMOSIS

The costs of a spiral wound cellulose acetate reverse osmosis system are presented. Costing assumptions are :

A. Unit investment, power, and operation and maintenance costs are based on permeate recovery of 95 per cent as applied to manufacturers' cost data in gal/hr of permeate recovery. Unit cost can vary depending on whether the unit is designed for chromium or nickel removal. The unit costs presented are for nickel removal.

B. Installation cost is considered negligible when compared to equipment cost and is not included in investment cost.

C. Total operation and maintenance cost includes system and pump maintenance, pump reconditioning, and a membrane replacement cost based on membrane life of 1 1/2 years.

Flow rate (liters/hr)	2,366	4,731	9,462
Investment ($)	25,129	38,658	60,569
Annual costs			
capital costs	1,603	2,466	3,864
depreciation	5,026	7,732	12,114
operation and maintenance costs (excluding energy and power costs)	4,873	9,675	20,761
Energy and power costs	1,404	2,144	3,536
TOTAL ANNUAL COST ($)................	12,906	22,017	40,275

EVAPORATION

ATMOSPHERIC EVAPORATION

Equipment for carrying out atmospheric evaporation is quite similar from one application to another. The major element is generally a packed column with an accumulator bottom.

Accumulated wastewater is pumped from the base of the column, through a heat exchanger, and back into the top of the column, where it is sprayed into the packing. At the same time, air drawn upward through the packing by a fan is heated as it contacts the hot liquid, which partially vaporizes and humidifies the air stream. The fan then blows the hot, humid air to the outside atmosphere. A scrubber is generally unnecessary because the packed column itself acts as a scrubber.

VACUUM EVAPORATION

Most vacuum evaporators equipment may be classified as submerged tube, climbing film, or flash evaporation units. The evaporated water is condensed in each of these approaches, and either single or double effect evaporation may be used.

In the most commonly used submerged tube evaporator, the heating and condensing coils are contained in a single vessel to reduce capital cost. The vacuum in the vessel is maintained by an eductor-type pump, which creates the required vacuum by the flow of the condenser cooling water through a venturi. Wastewater accumulates in the bottom of the vessel, and it is evaporated by means of submerged steam coils. The resulting water vapor condenses as it contacts the condensing coils in the top of the vessel. The condensate then drips off the condensing coils into a collection through that carries it out of the vessel. Concentrate is removed from the bottom of the vessel.

The major elements of the climbing film evaporator are the evaporator, the separator, the condenser, and the vacuum pump. Wastewater is "drawn" into the system by the vacuum so that a constant liquid level is maintained in the separator. Liquid enters the steam-jacketed evaporator tubes, and part of it evaporates so that a mixture of vapor and liquid enters the separator. The design of the separator is such that the liquid is continuously circulating from the separator to the evaporator. The vapor entering the separator flows out through a mesh entrainment separator to the condenser, where it is condensed as it flows down through the condenser tubes. The condensate, along with any entrained air, is pumped out of the bottom of the condenser by a liquid ring vacuum pump. Thus, the liquid seal provided by the condensate keeps the vacuum in the system from being broken.

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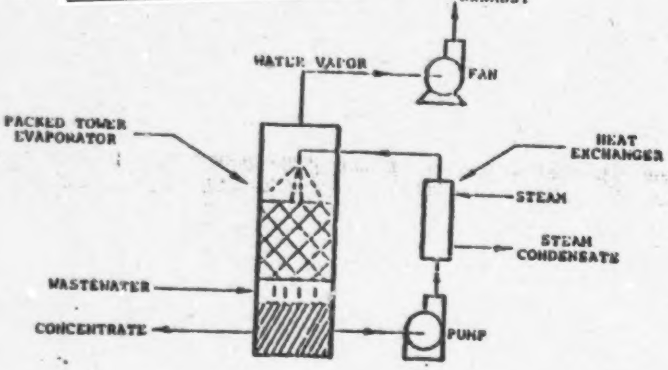
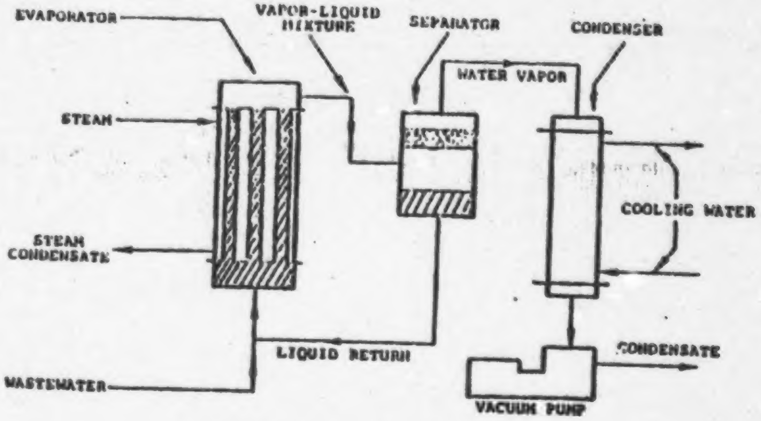
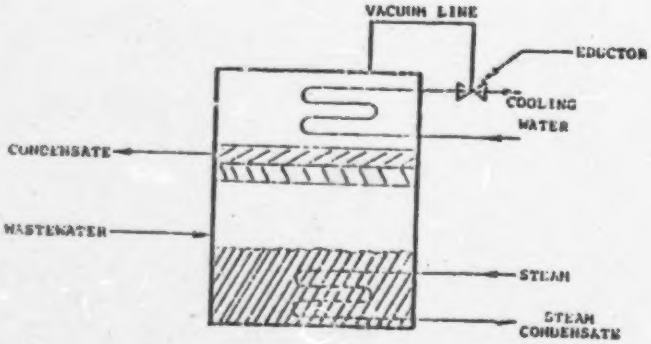

EXHAUST
WATER VAPOR
FAN
PACKED TOWER EVAPORATOR
HEAT EXCHANGER
STEAM
STEAM CONDENSATE
WASTEWATER
CONCENTRATE
PUMP

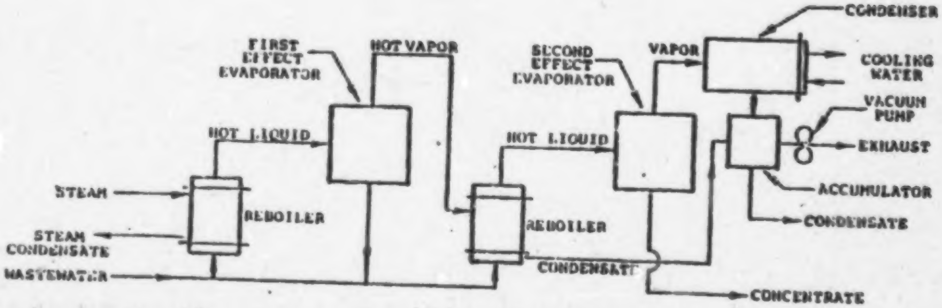
ATMOSPHERIC EVAPORATOR


EVAPORATOR
VAPOR-LIQUID MIXTURE
SEPARATOR
CONDENSER
WATER VAPOR
STEAM
COOLING WATER
STEAM CONDENSATE
CONDENSATE
LIQUID RETURN
WASTEWATER
VACUUM PUMP

CLIMBING FILM EVAPORATOR


VACUUM LINE
EDUCTOR
COOLING WATER
CONDENSATE
WASTEWATER
STEAM
STEAM CONDENSATE

SUBMERGED TUBE EVAPORATOR


CONDENSER
FIRST EFFECT EVAPORATOR
HOT VAPOR
SECOND EFFECT EVAPORATOR
VAPOR
COOLING WATER
VACUUM PUMP
HOT LIQUID
HOT LIQUID
EXHAUST
STEAM
REBOILER
REBOILER
ACCUMULATOR
CONDENSATE
STEAM CONDENSATE
WASTEWATER
CONDENSATE
CONCENTRATE

DOUBLE-EFFECT FLASH EVAPORATOR

TYPES OF EVAPORATION EQUIPMENT

./...

The main elements of the flash evaporator system are the evaporator, the reboiler, and the condenser.

The evaporator is an empty tank maintained at a pressure below that in the reboiler. Wastewater fed to the base of the evaporator circulates through a thermosiphon reboiler. The liquid heated in the reboiler re-enters the evaporator at a temperature above the boiling point corresponding to the evaporator pressure. Part of the liquid evaporates (flashes), and the resulting vapor goes out the top of the evaporator to the horizontal condenser, while the condensate runs into an accumulator from which it is pumped out of the system. A vacuum pump maintains the reduced pressure in the system by withdrawing noncondensible gases from the condenser. Concentrate is withdrawn from the bottom of the evaporator.

There is no fundamental limitation on the applicability of evaporation. There aren however, certain practical limitations for most types. For example, climbing film evaporation is used for acid copper plating solutions but not for cyanide copper because the materials of construction in current use are appropriate only for acidic conditions. However, both atmospheric and submerged tube evaporators are used for cyanide copper, and there is no reason why climbing film evaporation could not be used after a suitable change in construction materials.

SUBMERGED TUBE EVAPORATION

Submerged tube evaporation costs are shown for single effect units and for double effect units. Costing assumptions are :

A. Unit size, power requirements, and operational expenses (less energy and power) are based on data supplied by the manufacturer for standard size units.

B. Investment cost includes the basic evaporator and bath purification device.

C. Evaporative heat of 583 cal/gram of wastewater is required for single effect units, and 292 cal/gram is required for double effect units. The heating value of fuel is assumed to be 10,140 cal/gram (Lower Heating Value (LHV), API of 30) with a heat recovery of 85 per cent.

D. A cooling water charge is not included in the operation and maintenance cost. A cooling water circuit is assumed to already exist for the plant.

E. The condensate is assumed to be pure with the percentage of condensate and concentrate flow split based on the manufacturer's operational manual.

SUBMERGED TUBE EVAPORATION - SINGLE EFFECT

Flow rate (liters/Hr)	95	379	757
Investment ($)	11,156	23,486	34,077
Annual costs :			
capital costs	712	1,498	2,174
depreciation	2,231	4697	6,815
Operation and maintenance costs (excluding energy and power costs)	1,678	6,713	13,427
Energy and power costs	6,048	20,117	37,815
TOTAL ANNUAL COST ($).............	10,669	33,026	60,231

SUBMERGED TUBE EVAPORATION - DOUBLE EFFECT

Flow rate (liters/Hr)	189	568	1,136
Investment ($)	19,424	35,039	50,841
Annual costs :			
capital costs	1,239	2,235	3,244
depreciation costs	3,885	7,008	10,168
Operation and maintenance costs (excluding energy and power costs)	1,678	5,035	10,070
Energy and power costs	6,048	15,844	29,270
TOTAL ANNUAL COSTS ($).............	12,850	20,123	52,752

CLIMBING FILM EVAPORATION

Climbing film evaporation costs are presented. Costing assumptions are :

A. Unit sizes and costs are based on data supplied by the manufacturer for unit capacities of 114 to 284 liters/hour. Multiple units are used as needed.

B. Investment cost includes the basic evaporator and a bath purification device.

C. Evaporative heat of 583 cal/gram of wastewater is required. The heating value of fuel is assumed to be 10,140 cal/gram (LHV, API of 30) with a heat recovery of 85 %.

D. The electrical requirement is based on three pump horsepower per evaporation unit.

E. A cooling water charge is not included. A cooling water circuit is assumed to already exist for the plant.

F. The condensate is assumed to be pure.

Flow rate (liters/Hr)	114	795	4,731
Investment ($)	27,559	104,470	600,090
Annual costs :			
capital costs	1,758	6,665	38,285
Depreciation	5,512	20,894	120,018
Operation and maintenance costs (excluding energy and power costs)	0	0	0
energy and power costs	5,533	37,106	220,522
TOTAL ANNUAL COST ($).............	12,803	64,665	378,825

ATMOSPHERIC EVAPORATION

Atmospheric evaporation costs are presented. Costing assumptions are :

A. Unit sizes are based on data supplied by the manufacturer for standard unit capacities of 379 to 3,407 liters/hr. Two units provide a capacity to 6,814 liters per hour, maximum.

B. Investment costs include the basic evaporator with mid-range corrosion protection applied to the equipment and with bath purification.

C. Evaporative heat of 583 cal/gram of wastewater is required. The heating value of fuel is assumed to be 10,140 cal/gram (LHV, API of 30) with a heat recovery of 85 per cent.

D. The electrical requirement is based on a fan system power requirement of 10 horsepower per 379 liters per hour.

E. A cooling water circuit is assumed to already exist for the plant, and the cost of cooling water is not included.

F. The condensate is assumed to be pure.

Flow rate (liters/Hr)	379	1,893	6,813
Investment ($)	20,430	45,967	143,008
Annual costs :			
Capital costs	1,303	2,933	9,124
Depreciation	4,086	9,193	28,602
Operation and maintenance costs (excluding energy and power costs)	155	155	155
Energy and power costs	18,443	92,213	331,968
TOTAL ANNUAL COST ($)...............	23,987	104,494	369,848

FLASH EVAPORATION

The cost for flash evaporation are presented. Costing assumptions are :

A. Unit cost is based on a chromic acid influent requiring fiberglass vessels and tantalum heat exchangers. Investment cost includes the basic evaporator and bath purification and is based on data supplied by the manufacturer.

B. Operation and maintenance cost includes the fuel requirements for the evaporator and electrical requirements for the pumps.

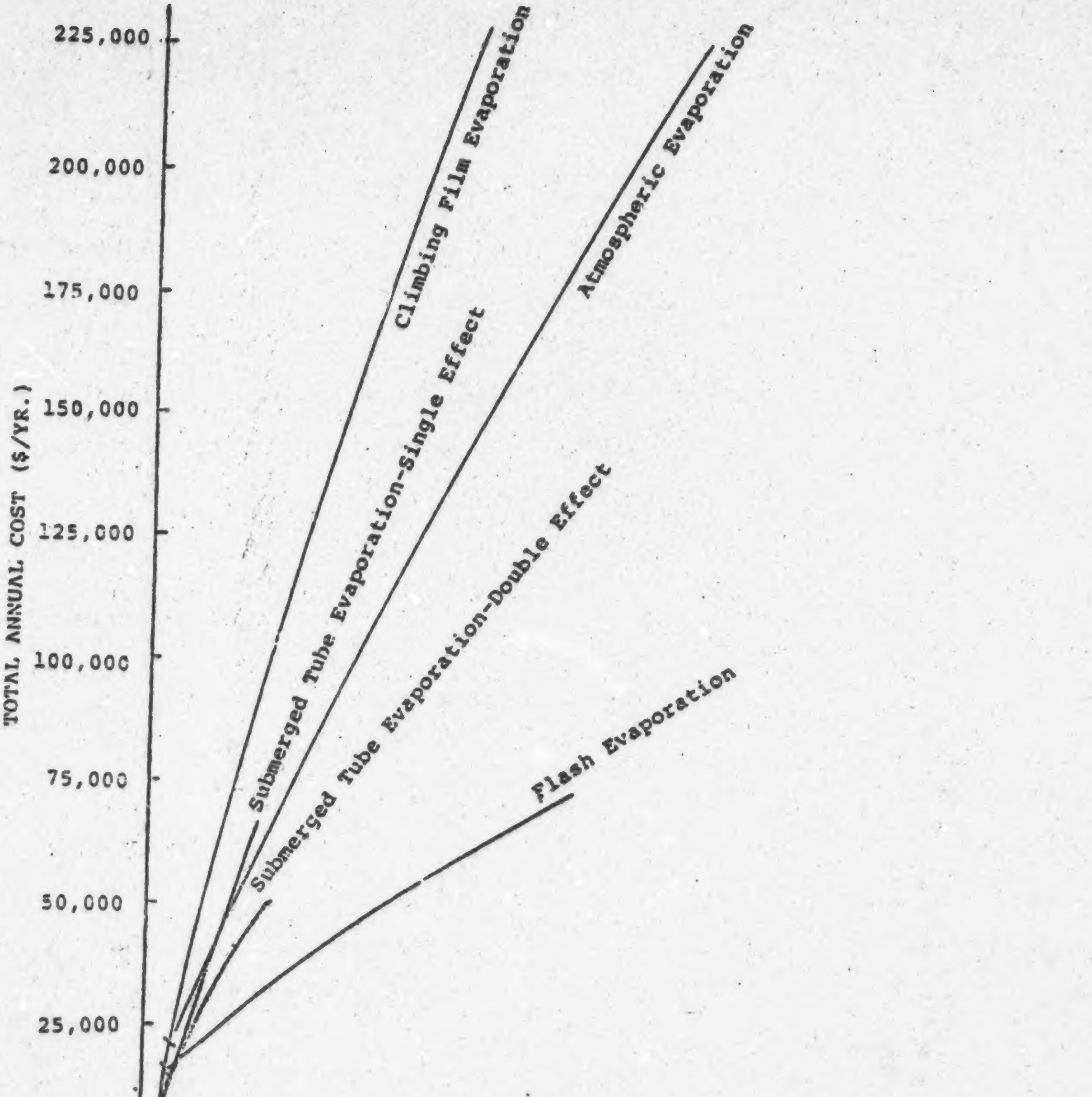
C. Evaporative heat of 583 cal/gram of wastewater is required. The fuel requirements are based on a heating value of 10,140 cal/gram (LHV, API of 30) and a heat recovery of 85 per cent.

D. The electrical requirement is based on a constant six kilowatts for the pumps.

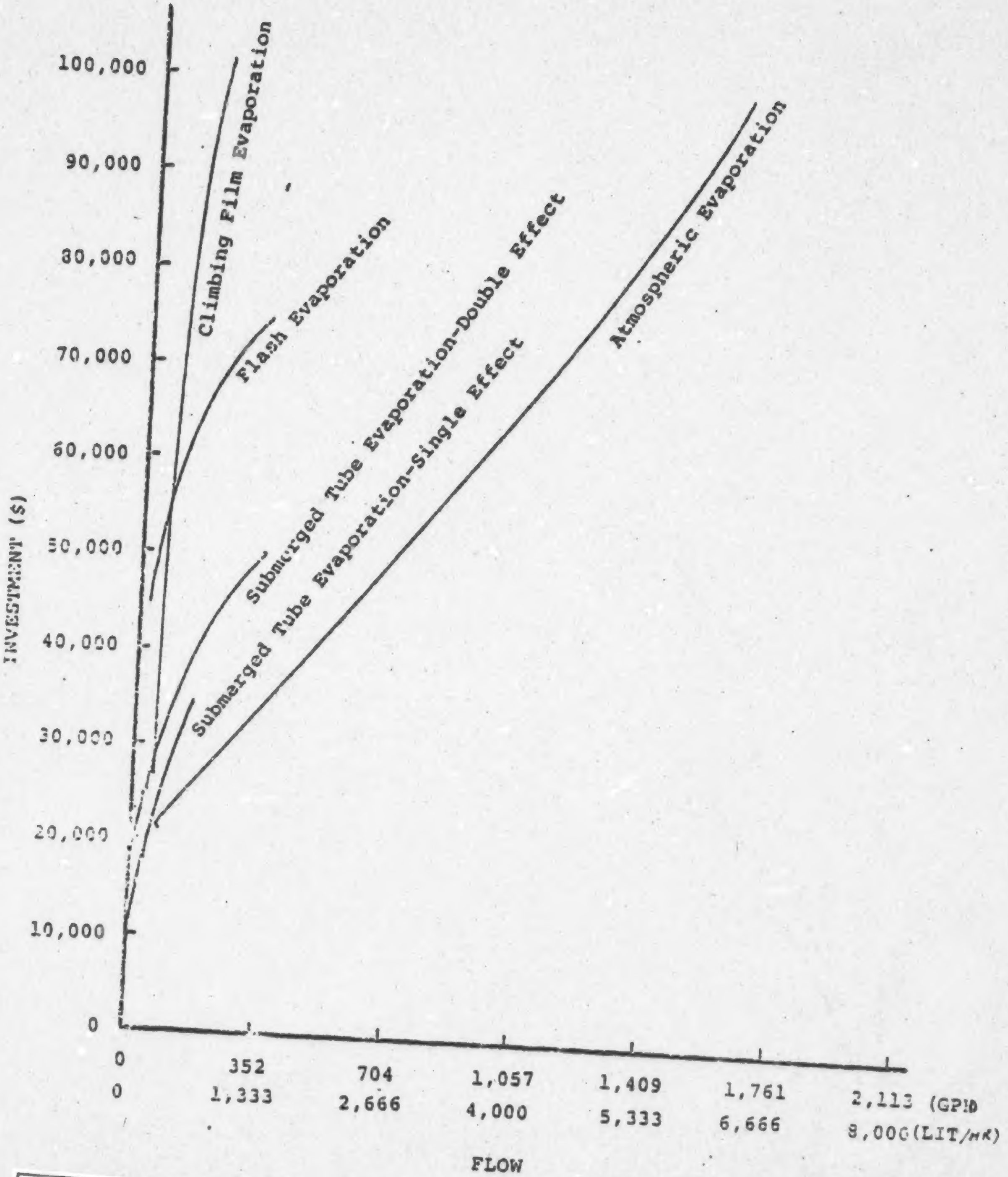
E. A cooling water circuit is assumed to already exist for the plant, and the cost of cooling water is not included.

F. The condensate is assumed to be pure.

Flow rate (liters/Hr)	189	568	1,136
Investment ($)	46,207	62,987	76,585
Annual costs :			
capital costs	2,948	4,018	4,886
depreciation	9,241	12,597	15,317
Operation and maintenance costs (excluding energy and power costs)	0	0	0
Energy and power costs	9,559	26,649	52,284
TOTAL ANNUAL COSTS ($)	21,749	43,265	72,487



EVAPORATION TOTAL ANNUAL COST



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EVAPORATION INVESTMENT COST

ANNEX B - APPENDIX 2

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CALCULATION OF RINSES :
Basing elements for problem solving

B.A.2.1. CALCULATION OF DRAG OUT

Qualitative aspect :

We shall assume that any fraction dragged out from a volume V represents the physico-chemical characteristics of this volume.

Quantitative aspect :

q flow dragged out in l/h

q is a function of : surface of slug
shape of a slug
supports
rate
straining
bath viscosity.

Estimates are made of the bath volume dragged out by a slug or by a group of slugs.

Added to this volume shall be the volume dragged out by the support (frame or drum)

B.A.2.1.1. Method of weighting

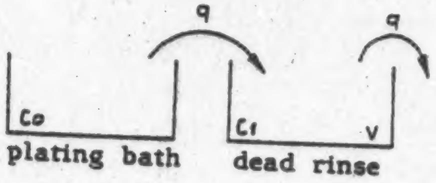
Assume that P_1 is the weight of the dry slug of surface S dm2
Assume that P_2 is the weight of this same slug after immersion and straining in a liquid density d.
The volume dragged out is such that : $\frac{P_2 - P_1}{d}$ which corresponds to a drag out E,

$$E = \frac{P_2 - P_1}{dS} \text{ l/dm2}$$

This method is very easy to apply to a continuous manufacturing of a limited number of slug types. In order to obtain an average value, a group of estimates should be calculated for baths having a different viscosity.

B.A.2.1.2: Methods of concentrations

Assuming V volume of water of an inactive rinse
n the transfer number
q the volume dragged out per unit of time (l/Hr)
E drag out l/dm2
S surface treated (dm2) corresponding to a transfer
T time corresponding to n transfers
Rd dilution ratio = $\frac{Co}{C_1}$
Co concentration in the bath
C_1 concentration in the dead rinse after n transfers



Summary of the weights :

$$V\ dCl = q\ Codt - Cl\ qdt$$

$$V \frac{dCl}{dt} + C_1 q = q\ Co$$

$$\frac{dCl}{dt} + \frac{q}{V} C_1 = \frac{q}{V} Co$$

The resolution of this differential equation of the first degree gives :

$$Cl = Co \left[1 - \exp\left(\frac{-qT}{V}\right)\right]$$

$$\exp\left(-\frac{qT}{V}\right) = \frac{Co - C_1}{Co}$$

$$\exp\left(\frac{qT}{V}\right) = \frac{Co}{Co-C_1} = \frac{1}{1 - \frac{Cl}{Co}}$$

$$\frac{qT}{V} = \log 1 - \log\left(1 - \frac{Cl}{Co}\right) = -\log\left(1 - \frac{Cl}{Co}\right)$$

Working out the log gives :

$$\frac{qT}{V} = \frac{Cl}{Co} + \frac{1}{2}\left[\frac{Cl}{Co}\right]^2 + \frac{1}{3}\left[\frac{Cl}{Co}\right]^3 + \frac{1}{4}\left[\frac{Cl}{Co}\right]^4 + \dots$$

$$qT = \frac{V}{Rd}\left[1 + \frac{1}{2Rd} + \frac{1}{3Rd^2} + \frac{1}{4Rd^3} + \dots\right]$$

Therefore $q = \frac{V}{T.\ Rd}\left[1 + \frac{1}{2\ Rd} + \frac{1}{3\ Rd^2} + \frac{1}{4\ Rd^3} + \dots\right]$

If we want to know drag out : $E.\ Sn = qT$

$$E = \frac{V}{S.n.Rd}\left[1 + \frac{1}{2\ Rd} + \frac{1}{3\ Rd^2} + \frac{1}{4\ Rd^3} + \dots\right]$$

Conclusion :

To find the drag out, we have only to measure the concentration C_1 in the dead rinse after n transfers.

Since V, Co, S are known, E is found by the above formula.

C_1 and Co must be expressed with the same units.

B.A.2.2. CALCULATION OF THE RINSING FLOW

B.A.2.2.1. General

After immersion in a liquid characterized by Co, the slug is covered by a liquid film having the same characteristics.

The function of rinsing is to substitute this film characterized by Co for a film characterized by C1 with $C1 < Co$.

The ratio $\frac{Co}{C1}$ is called DILUTION RATIO = Rd

Co being a known value (bath), the ideal would be, then, to be able to determine for each rinse the optimum value of C1.

The determination of C1 depends on the requirements of the rinsing function, but also on the need to protect the following bath.

Assuming a bath of concentration Co.

The rinsing function is to give a dilution ratio $Rd = \frac{Co}{Cn}$ where Cn is the concentration of water covering the slug when it is transfered into the next bath.

The ratio Rd may be obtained either by one or by n dilutions such as :

$$\frac{Co}{Cn} = \frac{Co}{C1} \times \frac{C1}{C2} \times \ldots \times \frac{Cn-1}{Cn}$$

- Either n = 1, then the concentration in rinsing water of additives issued from the plating bath is necessarily very low (see flow calculation)

- or $n > 1$, then the concentration of the n rinsing baths decreases from C1 to Cn.

In the case of a parallel collect of rinsing waters, n effluents are obtained which concentrations are C1, C2,....Cn.

In the case of a cascade scheme, only one effluent of concentration C1 is obtained.

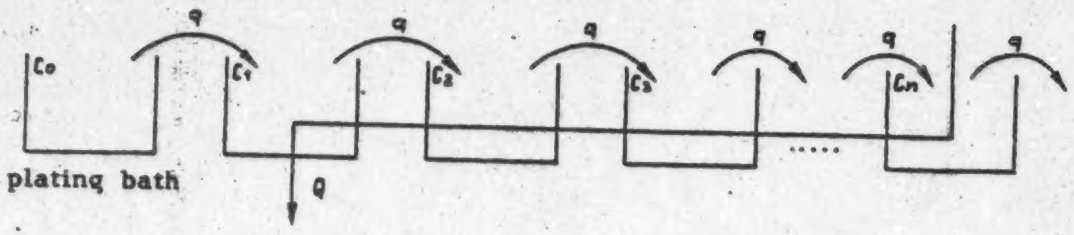
So, if $n > 1$, the effluent concentration C1 could be very near of C0.

Accordingly, the number and the design of rinses may be imagined in order to obtain effluents which concentrations are compatible with :

- direct recovery from the plating bath
- recovery after concentration
- end-of-pipe detoxification
- recovery by ion exchange.

B.A.2.2.2. Calculations

a) Assuming n cascade rinses :



Summary of weights :

For rinse N° 1 : $qCo + Qc2 = (Q + q)C1$

For rinse N° 2 : $qC1 + Qc3 = (Q + q)C2$

For rinse N° 3 : $qC2 + QC4 = (Q + q)C3$

- -

n-1 : $qCn\text{-}2 + QCn = (Q + q)\ Cn\text{-}1$

n : $qCn\text{-}1 = (Q + q)\ Cn$

total line by line : $qCo = QC1 + qCn$

$$qCn\text{-}1 = (Q + q)\ Cn$$
$$qCn\text{-}2 = (Q + q)\ Cn\text{-}1\text{-}QCn$$
$$q^2Cn\text{-}2 = q(Q + q)\ Cn\text{-}1 - qQCn$$
$$= (Q - q)^2\ Cn - qQCn$$
$$= (Q^2 + qQ + q^2)\ Cn$$
$$qQn\text{-}3 = (Q + q)\ Cn\text{-}2 - QCn\text{-}1$$
$$q^3Cn\text{-}3 = q^2\ (Q - q)\ Cn\text{-}2\text{-}q^2QCn\text{-}1$$
$$= (Q + q)\ (Q^2 + qQ + q^2)\ Cn - qQ\ (Q - q)\ Cn$$
$$= (Q^3 + Q^2q + q^2Q - q3)\ Cn$$

Therefore

$$q^x\ Cn - x = (Q^x + Q^{x-1}q + Q^{x-2}q^2 + \ldots + q^2)\ Cn$$

Estimate of C1 ;

$$x = n\text{-}1$$
$$q^{n-1}\ C1 = (Q^{n-1} + Q^{n-2}q + \ldots\ldots + q^{n-1})\ Cn$$
$$qCo = QC_1 = qCn$$
$$q^n\frac{Co}{Cn} = q^{n-1}Q\ \frac{C1}{Cn} + q^n$$

$$q^n \frac{Co}{Cn} = Q \; (Q^{n-1} + Q^{n-2}q + \ldots + q^{n-1}) \; q^n$$

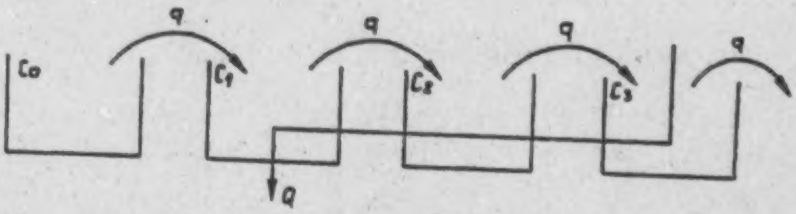
Assuming general formula :

$$q^n Rd = Q^n - Q^{n-1}q + Q^{n-2}q^2 + \ldots + q^n$$

Application example with :

$Co = 400$ g/l
$q = 12$ l/h
$Rd = 20{,}000$

Assuming the modulus : 3 cascade rinses

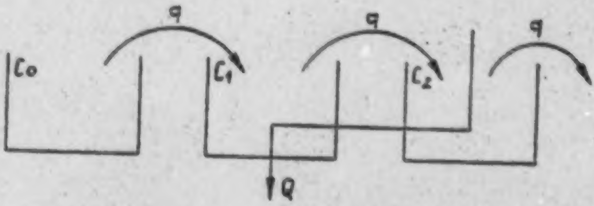


The general formula applies here with n = 3

$$q^3 Rd = Q^3 + Q^2 q + Qq^2 + q^3$$

Therefore : Q = 322 l/hr and C1 = 13.9 g/l
C2 = 0.55 g/l
C3 = 0.02 g/l

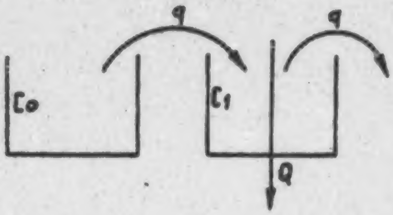
Assuming the modulus : 2 cascade rinses



n = 2 : $q^2 \; Rd = Q^2 + Qq + q^2$

Therefore Q = 1690 l/hr and C1 = 2.84 g/l
C2 = 0.02 g/L

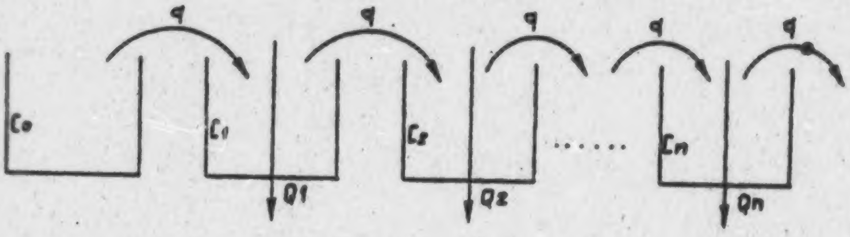
Assuming the modulus : 1 cascade rinse



$n = 1$: $qRd = R + q$

Therefore : $Q = 240{,}000$ l/hr and $C1 = 0.02$ g/l

b). Assuming n parallel rinses :



Summary of weights :

Assuming $Rdn = \frac{Cn-1}{Cn}$

For rinse N° 1 : $qRd1 = Q1 + q$
$q(Rd1-1) = Q1$

1 is negligible in front of Rd

Therefore : $qRd1 = Q1$

For rinse N° 2 : $qRd2 = Q2$

……

For rinse N° n : $q\,Rdn = Qn$

$Rd = Rd1 \times Rd2 \times \ldots \times Rdn$

Therefore $q^n.Rdn = Q1 \times Q2 \times \ldots. \times Qn$

REMARKS

1 - To obtain a given dilution ratio (Rd) with n rinses, the total rinse flow is :

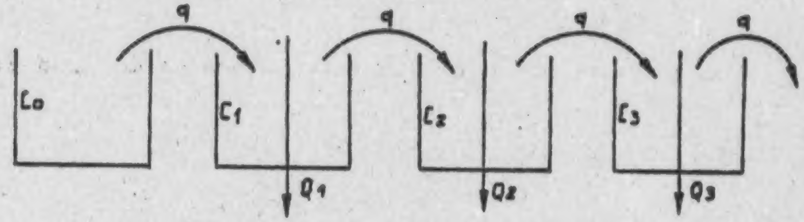
$$Q1 + Q2 + ...Qn = q\ (Rd1 + Rd2 ...+ Rdn)$$

This sum is minimum when :

$$Q1 = Q2 = ... Qn$$

i.e. when $Rd1 = Rd2 = Rd3 = ... = Rdn = Rd^{\frac{1}{n}}$

Assuming the modulus :



To obtain a minimal water consumption

$$Rd1 = Rd2 = Rd3 = \sqrt[3]{20\ 000}$$

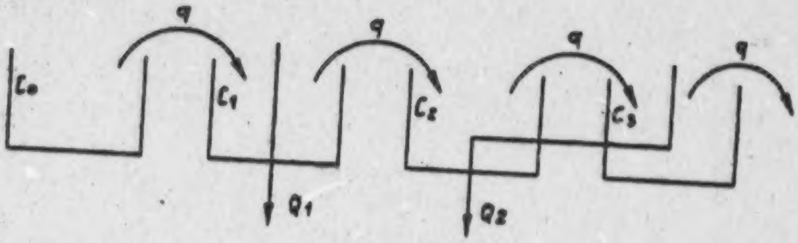
therefore $Q1 = Q2 = Q3 = qRd1 = 326$ l/hr

$C1 = 14.7$ g/l
$C2 = 0.54$ g/l
$C3 = 0.02$ g/l

2 - In the case of n cascade rinses, only one rinse flow may be selected because of the given value of Rd. On the other hand, if these n rinses occur in parallel, or if some of them occur in parallel (Qp) and others in cascade (Qc), it is then possible to find an infinity of values of Qp and Qc for a single and same value of Rd.

c) Mixed arrangement :

Given the modulus :



Two supply and recovery circuits are arranged here with flows Q1 and Q2, each circuit having two dilution ratios :

$\text{Rd1} = \frac{\text{Co}}{\text{C1}}$ and $\text{Rd2} = \frac{\text{C1}}{\text{C3}}$

It is thus possible to select different values of Rd1 and Rd2, so that we always have :

$\text{Rd1} \cdot \text{Rd2} = \text{Rd} = 20\ 000$

We have (see above) :

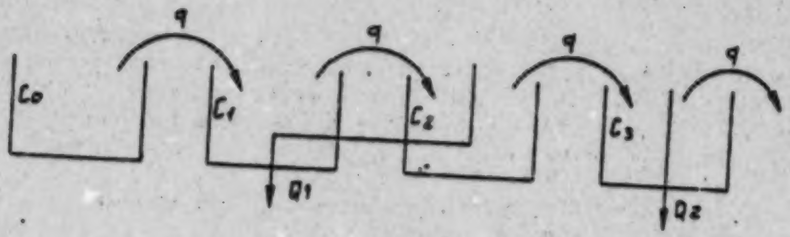
$$\text{Rd1} = \frac{\text{Q1}}{q}$$

$$\text{Rd2} = \frac{\text{Q2} + \text{Q2}q + q^2}{q^2}$$

Numerical applications :

q	Co	Q_1	Rd1	C_1	Rd2	Q_2	C_2	C_3
12	400	100	9	42,85	2142	548	0,93	0,02
		200	17	22,64	1132	396	0,68	0,02
		300	26	15,38	769	325	0,56	0,02
		400	34	11,65	582	282	0,49	0,02
		500	42	9,37	468	252	0,44	0,02
		600	51	7,84	392	230	0,40	0,02
		700	59	6,74	337	213	0,37	0,02
		800	57	5,91	295	199	0,35	0,02
		900	76	5,26	263	187	0,33	0,02
		1000	84	4,74	237	177	0,31	0,02

Assuming the modulus :



$$Rd1 = \frac{Co}{C_2} = \frac{Q_1^{\,2} + Q1_q + q^2}{q^2}$$

$$Rd2 = \frac{C_2}{C_3} = \frac{Q_2}{q}$$

Numerical applications :

q	Co	Q1	Rd1	C_1	C_2	Rd2	Q2	C_3
12	400	100	78	47,39	5,07	253	3034	0,02
		200	295	23,91	1,35	57	800	0,02
		300	651	15,97	0,61	30	356	0,02
		400	1145	11,98	0,34	17	197	0,02
		500	1178	9,59	0,22	11	122	0,02
		600	2551	7,99	0,15	7	82	0,02
		700	3462	6,85	0,11	5	57	0,02
		800	4512	5,99	0,08	4	41	0,02
		900	5701	5,33	0,07	3	30	0,02
		1000	7028	4,79	0,05	2	22	0,02

3 – The above calculations assume as a beginning hypothesis :

- a continuous transfer (q) from the bath into the rinse, q being independent of the concentration and the viscosity to simplify the calculations,
- an average concentration C_R in the rinse.

These hypotheses are perfectly acceptable when applied to effluent treatment, except in rare cases.

This is not the case, however, for the metal finishing itself.

In fact, if the transfer is very discontinuous, and if the homogenization in the rinse is not good (absence of air diffusion, hollow slugs, large liquid absorption at the surface of the slug, quenching too fast, etc...), there will be gaps between the calculation and its application.

Accordingly, this risk should be evaluated and the appropriate control should be determined.

4 - The dilution ratio has been defined as :

$$Rd = \frac{Co}{Cn}$$

Co and Cn are respectively the total bath concentration and Cn the total concentration of the last rinse.

Thus, some cases should not be based on the total concentration, but on the bath constituents, for it shall be necessary to protect the following bath from this constituency.

This is particularly the case of some products used in activation baths on ABS which are highly hazardous for the following deposit baths.

ANNEX B - APPENDIX 3

....

COMPARISON OF THE ION EXCHANGER RECYCLING PROCESS (A) AND THE MULTIPLE CASCADE (B) RINSE TECHNIQUE

TECHNICAL ASPECTS :

Conditions of comparison

- same rinsing efficiency,
- analogous concentration of effluents obtained :
  - for A : regenerated eluate,
  - for B : effluent.

Terms of comparison

- water consumption,
- concentration of effluents obtained.

COMPARISON :

Origin of consumptions

(A) a : circuit filling
b : evaporation
c : eluate

(B) d : evaporation
e : effluent

a,b,d, negligible - hence, c and e are to be compared.

Basic data

a) concentration (Cx)

$o \leqslant x \leqslant n$

expressed in equivalents /liter

b) drag out

flow : q in l/hr
hence products : q X c in equiv./hr

c) Rinsing efficiency

Dilution ratio : $Rd = \frac{Co}{Cn}$

d) Fixation on ion exchangers (cations and anions)

base : 1 equiv. fixation/liter of resin
or for 1 salt equiv., a resin saturation of 2 l.

e) Rate of recycling

Period between regenerations (cycle) X hours
Hence, salinity fixation per cycle :
qCox equiv. cations
qCox equiv. anions
Assuming a saturation of :
qCoX liters C and
qCoX liters A
Then, basic recycling ratio Q_R = 20 volumes/volume of resin/hr,
Therefore :

$$Q_R = 20\ qCo_X$$

f) Limits

- resin volume per device :
  - maximum : 5,000 l
  - minimum : 100 l
- average bath concentration :
  $Co \leqslant 4$ equiv./l
  base Co = 2 equiv./l
- drag out :
  average : $1 < q < 10$ l/hr
- cycles :
  X maximum = $\frac{5{,}000}{qCo}$ with Co = 2 and $1 < q < 10$
  therefore 250 hr X maxi = 2,500 hr
  X minimum = $\frac{100}{qCo}$ therefore 5 < mini < 50 hr.

Technically, it appears necessary to select :

$$5\ \text{hr} < X < 250\ \text{hr}$$

Then, $Q = 20\ qCoX$

$$\frac{Q}{q} = R_D = 20\ CoX$$

which gives us : $200 \leqslant R_D \leqslant 10{,}000$

. Eluate volume i.e. maximum water volume consumed by the regeneration of one liter of resin : 10 l loosening reactive dilution and rinse.

. water consumption as a function of salinity dragged out (A) for qCo equiv. of salt dragged out/hr

$$Q_A = 20\ qCol/hr$$

(B) $q^n R_D = Q_B{}^n + qQ_B{}^{n-1} + \ldots\ldots q^n$

hence approximating by default : $Q_B = q\sqrt[n]{R_D}$

i.e.

$$Q_B = q\sqrt[n]{\frac{Co}{Cn}}\ \ l/h$$

Estimate :

For a period X, and always for $R_D = \frac{Co}{Cn}$

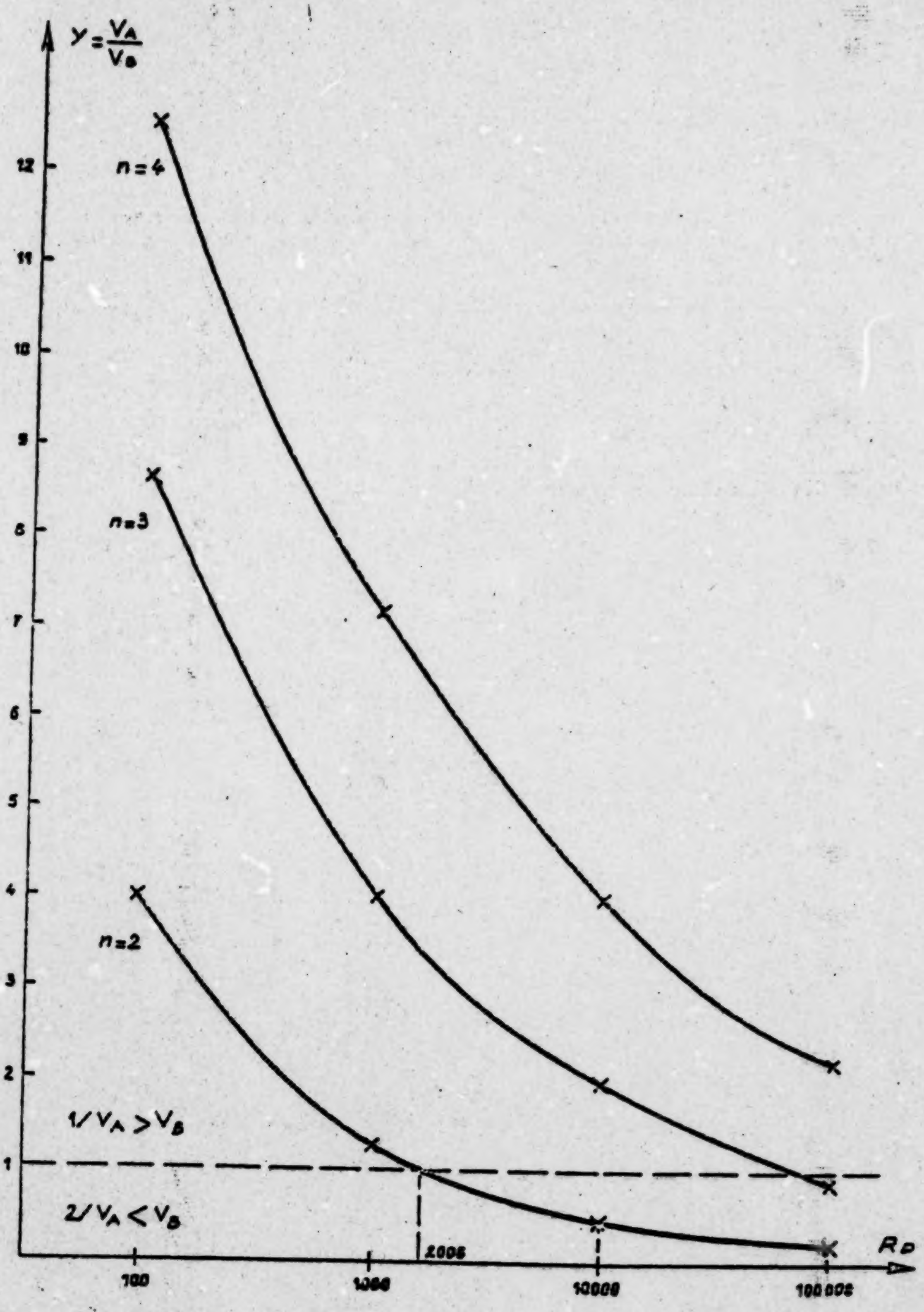
$$\frac{V_A}{V_B} = \frac{20\ \ qCnR_DX}{q\sqrt[n]{\frac{Co}{Cn}}} \quad \text{or} \quad \frac{V_A}{V_B} = \frac{20\ Co}{\sqrt[n]{R_D}}$$

If $Co = 2$

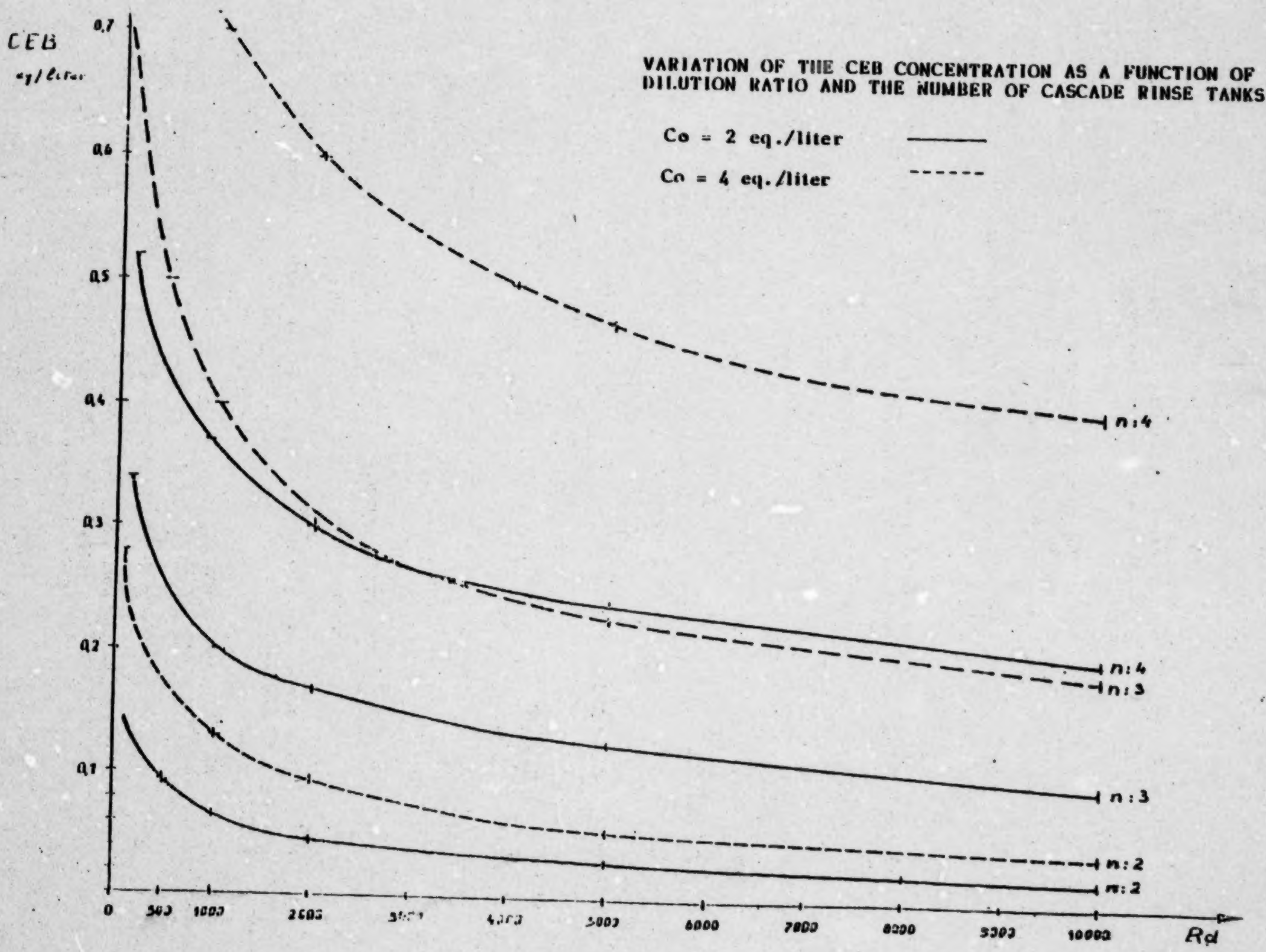
$$\frac{V_A}{V_B} = \frac{40}{\sqrt[n]{R_D}}$$

Therefore for : $n = 2$
$n = 3$
$n = 4$

and $100 < R_D < 100{,}000$, we obtain the graphs shown below :



$Y = \frac{V_A}{V_B}$
12
11
10
9
8
7
6
5
4
3
2
1
n = 4
n = 3
n = 2
1/ $V_A > V_B$
2/ $V_A < V_B$
2000
100
1000
10000
100000
R_D



VARIATION OF THE CEB CONCENTRATION AS A FUNCTION OF THE DILUTION RATIO AND THE NUMBER OF CASCADE RINSE TANKS

CONCLUSIONS

■ With respect to water consumption, a system of n cascade rinses with $n \gg 3$ is therefore always more advantageous than the recycling on ion exchangers.

Just as interesting may be the case for n = 2 when $2{,}000 < R_D < 10{,}000$, but the technical simplicity of (E) could be determining, especially when the facilities are new.

In fact, the multi-rinse concentration procedure requires no energy, no reagent and practically no maintenance.

■ As for the effluents obtained, the comparison of their respective concentrations gives the following results :

- SYSTEM A : effluent concentration : $\dfrac{\text{drag out}}{\text{volume of eluates}}$

given $\dfrac{qC_o \text{ equiv./hr}}{V_A \text{ l/hr}}$

i.e. : $\dfrac{qC_o}{20\, qC_o} = \dfrac{1}{20}$ equiv./l

$$C_{EA} = 0.05 \text{ equiv./l}$$

- SYSTEM B : effluent concentration : $\dfrac{\text{drag out}}{\text{water consumption}}$

given $\dfrac{qC_o \text{ equiv./l}}{V_B \text{ l/hr}}$

i.e. : $\dfrac{qC_o}{q\sqrt[n]{R_D}}$

$$C_{EB} = \frac{C_o}{\sqrt[n]{R_D}} \text{ equiv./l}$$

This means, the,, that C_{EA} is limited to a maximum concentration threshold of 0.05 equiv. salt/l approximately, whereas C_{EB} may reach Co.

5 The installation of multiple rinses is sometimes impossible for the following practical reasons :

-impossibility to modify an existing structure,
-lack of space,
-additional work load (for manual set up),
-bulky slugs (impossible to handle several times),
-rarely for chemical reasons.

ANNEX B - APPENDIX 4

oooooooooo

NEW TECHNIQUES
AND
NEW APPLICATIONS OF CONTROL TECHNIQUES

B.A.4.1. RINSING

Jet rinse or spray rinse, which may be combined with suction, presents many advantages, especially in the case of zinc plating, copper plating or nickel plating in the drum :

- decrease in water consumption ;
- a semi-concentrated effluent is obtained, therefore the cost of concentration prior to recycling the solution into the plating bath is reduced ;
- no or less static recovery rinses : 99 % of drag out being recovered by spray rinse.

This process is widely sold. (cost : refer to rinse, appendix 1 of this Annex).

B.A.4.2 ION EXCHANGERS

B.A.4.2.1. ECO-TEC Licence

ECO-TEC ion exchangers alternatively use a cation exchange resin and a combination of anion exchange resins, and have the following characteristics :

- Rapid cycling which allows for a full automatic unit to achieve a continuous work ;

- a maximized surface area by using fine resins, what increases again the exchange rate ;

- much smaller pieces of equipment when compared with conventional ion exchange.

This process is employed for recovery of chromic acid, nickel and other heavy metals.

The economics of ECO-TEC system are favorable.

For example, installation of a system recovering 5 kg/hr of nickel salts can result in paying back on capital investment as short as less than 8 months.

(cost : refer to cyclic ion exchanges, appendix 1 of this Annex).

B.A.4.2.2. Purification of chromic acid

Bayer SNL-63 type resins allow the purification of chromic acid from aluminium anodizing. Al^{+3} cations (Ni^{2+} too) are held by the resin, and purifyed chromic acid may be recycled into the anodizing bath.

B.A.4.2.3. Recovery of phosphoric acid

A selective ion exchange process allows the recovery of the phosphoric acid used in the finishing treatments of aluminium.

The acid of a solution which also contains its salt is absorbed preferably on a strong basic ion exchange resin.

The acid is then eluted with water ; this process is economical, but the technology must be improved.

B.A.4.3. EVAPORATION

B.A.4.3.1. New applications

A new fine film evaporator which recompresses steam allows the recovery of chromic acid. By applying this process, the chromic acid consumption decreases by 80 % and its effluent content is lowered by 99.98 %.

The main obstacle to using the evaporation procedure is a high energy consumption :there is a process working at low temperature and close to air pressure by using recovered heat.

It has been applied for the recovery of phosphates.

B.A.4.3.2. Freeze separation

Thermodynamic energy requirements for separation by freezing are less than for evaporation (80 kcal/l instead of 540 kcal/l).

Accordingly, this process should be developed. As large investments are required for putting in such a unit, its use is practical only in large facilities.

The effluents are cooled to a point of freezing by evaporation of a hydrocarbon at low boiling point (propane). The gaseious hydrocarbon is recovered, recompressed to liquefaction and recycled.

Relatively pure water is obtained through solid and liquid phase separation and through ice melting. The solution containing the impurities is concentrated.

One freezing unit must be used on each plating or rinsing bath, as for evaporation or reverse osmosis.

B.A.4.4. REVERSE OSMOSIS AND MEMBRANE TECHNIQUES

B.A.4.4.1. Reverse osmosis

Laboratory tests with a new NS-100 membrane constituted with polyethyleneimine and tolylene diisocyanate, demonstrated its sustained performance from pH = 1 to pH = 13.

B.A.4.4.2. Ultra filtration

This is both a filter and use of reverse osmosis. The "modulus" is generally used only under a pressure of 3 to 8 bars (instead of 20 to 30 bars) and allows for the passage of water, solubilized salts and micromolecular substances. In the concentrate recovered , there are oils, solid particles and micromolecular organic substances.

A recent system, with a specially adapted plastic-coated modulus containing porous graphite, permits ultra-filtration to be accomplished in a pH zone ranging between 1 and 14 and at a temperature ranging from ambient to 95° C.

Furthermore, the system includes a closed circuit balanced by a batcher which compensates in the solution of the bath to be filtered the amount of ultrafiltrate which passes through the modulus. The closed circuit becomes progressively concentrated in impurities and very small amounts of highly concentrated materials are discharged.

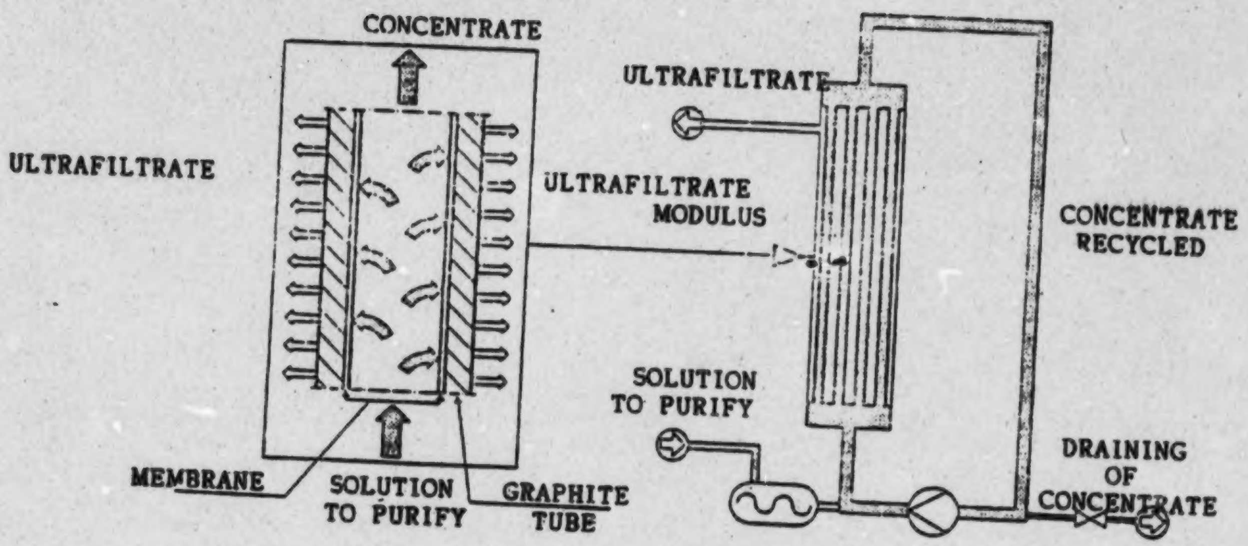
The ultra-filtrated water cannot be directly recycled in this case either. For complete purification to be accomplished, a passage on ion-exchangers must occur. This process is used only as a concentrator.

On the other hand, the system may be utilized effectively for a degreasing or an amorphous phosphatation.

The active bath is recycled continuously through the ultra-filtration device and the filtrate turns the bath. The concentrate, which constitutes only a few liters per week, is treated (frequently by incineration, as the oil content is high).

The recycled bath retains its qualities much longer and discharge of the bath waste is avoided - and this in the ratios of 12/1 to 50/1.

It is nevertheless necessary to concentrate the ultrafiltrated baths with products different than their constituency to balance the substances which pass through or which are kept in the modulus, depending on the size of their molecules.


CONCENTRATE
ULTRAFILTRATE
ULTRAFILTRATE
ULTRAFILTRATE
MODULUS
CONCENTRATE
RECYCLED
SOLUTION
TO PURIFY
DRAINING
OF
CONCENTRATE
MEMBRANE
SOLUTION
TO PURIFY
GRAPHITE
TUBE

B.A.4.4.3. New membrane techniques

The Donnan dialysis uses only a concentration difference and no other form of energy. The waste waters containing metallic ions (nickel) pass into a tube with a small diameter, the walls of which are made by an ion exchanger membrane. A regenerating liquid (sulphuric acid) circulates against this current on the other side of the membrane. This process produces a slightly acid water. The DU PONT production of the Nafion perfluorided resin has allowed for the manufacture of a cation exchange membrane having an exceptional chemical resistance and good mechanical properties which are tested for nickel recovery.

Another process uses a liquid membrane, i.e. a solution complexing agent in an organic solvent is closed in a microporous membrane, usually made of polypropylene. The metal is complexed at the surface of the membrane, passes through it in this form thanks to the concentration gradient, and is liberated at the other side by pH variation. The complexing agent is thus regenerated and the procedure may continue.

This process appears to be highly advantageous for the treatment of chromium and copper, but it is, at present, only in its first stage of development.

B.A.4.5. ELECTROLYSIS

B.A.4.5.1. VALCLA cells

Positive recovery conditions are obtained by coupling a high circulation velocity with the creation of numerous turbulences by the application of anodes in expanded metal.

The recovery of precious metals is performed on two half-cathodes made of stainless steel. In a cyanided medium, gold and silver have an extraction limit of 0.1 mg/l.

The cells of non ferrous metal recovery are characterized by a piling of anodes and cathodes using a press filter or plate exchanger type mounting. In a sulphate medium, the copper has an extraction limit of 50 mg/l. Nickel in a sulphate medium and cadmium in a cyanided medium have an extraction limit of about 1 g/l. The energy consumed varies from 1 to 5 Wh/g for gold, silver and copper and ranges from 20 to 25 Wh/g for nickel and cadmium.

B.A.4.5.2. Chromic acid recovery

Chromic acid baths, either for chromium plating or for chromatizing, are polluted by trivalent chromium. Electro-chemical recovery is possible.

An american process consists of oxidizing trivalent chromium on a lead anode whereas hydrogen is given off at the nickel cathode. The yield is 80 % when trivalent chromium concentration is higher than 5 g/l. It is operating full scale.

A dutch process is integrated in the plating chain. The chromium plating bath is restored on a cation membrane. Trivalent chromium is oxidized on a titanium lead dioxide anode whereas pollutants as Zinc II are reduced to insoluble metal on the cathode. Recovered baths have the same properties as a new bath.

B.A.4.6. ELECTRO-ELECTRODIALYSIS

Application for the recovery of chromic acid.

Electro-electrodialysis (EED) is the means by which electric energy may be used to develop unspontaneous physico-chemical reactions.

This is accomplished by combining equitably in an appropriate cell the role of the electrodes together with that of the ion exchange membranes.

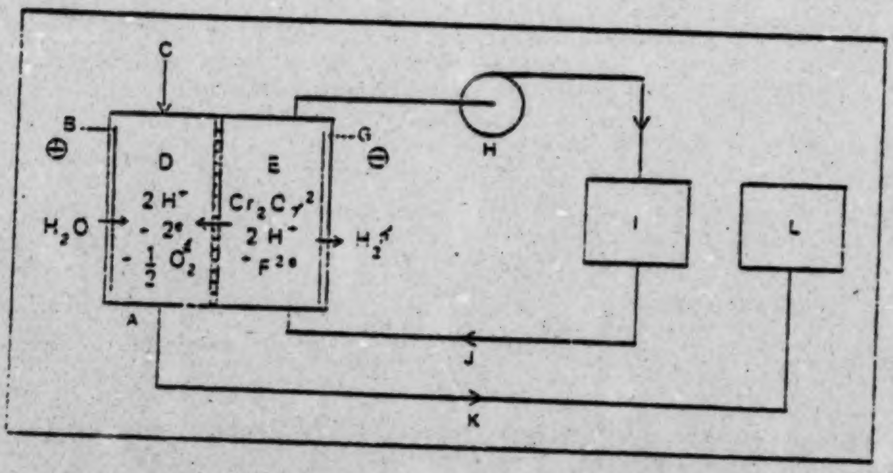
The design of the E.E.D. cell depends on the problem treated. In the special case of chromium plating shops, the latter is presented in terms of purification and concentration simultaneous with a rinse liquor after chromium plating, which is polluted by metallic cations, for example, and essentially made up of a chromic acid diluted solution with a pH of about 2 :

strong electrolyte of chemical formula : $Cr_2O_7^{=} + 2\ H^+$

Provided that an anion exchange membrane is placed as separator between anolyte and catholyte, it is in fact theoretically possible to conceive of an E.E.D. cell operating in accordance with the reactive diagram below :

$$H_2O + Cr_2O_7^{2-} + 2\ H^+ + \text{impurities} \xrightarrow{\text{membrane}} Cr_2O_7^{2-} + \tfrac{1}{2}O_2 + H_2$$

It may be observed that water and electric energy are required to purify and concentrate chromic acid, which may then be reused ; whereas hydrogen and oxygen are by-products of electrolysis.



A - E.E.D. cell
B - anode
C - Water
D - anolyte
E - catholyte
F - anionic membrane
G - cathode
H - filter pump
I - rinse bath
J - impure and diluted solution
K - purified solution -concentr
L - electrolysis bath

It is shown that the electric energy thus consumed, if the electrode shape and arrangement are appropriate, may be broken down :

- to bring about electrochemical reactions specific of oxidation and water reduction ;

- to ensure the migration of the anion $Cr_2O_7^=$ through the separator from the catholyte to the anolyte ;

- to permit the migration of ions into each of the two compartments of the cell thus subjected to the Joule effect, which is a natural heat source, hence additional asset for quality rinsing ;

- to refine by electro-osmosis the impurities "trapped" in a cathodic sheating from which they shall be extracted partially dewatered. This gives parameters for research and design optimimization of a prototype cell integrated into a production ring. From this study, it has been brought to light that such a machine can be designed in terms of a physical model with a closed system in which the total number of anionic equivalents Cr_2O_7 is maintained by :

$$C_A V_A + C_C V_C = \text{constant}$$

where V_A is the volume of anolyte with concentration equivalent C_A

V_C is the catholyte volume of concentration equivalent C_C

The anolyte concentration satisfies the following equation :

$$V_A . dC / dt = I/F\ (1 - t^+), \qquad \text{with } t^+ = t_o^+ + k.C_A$$

where t^+ represents the unit complement of the number of conveyances of the anion in the membrane and may be interpreted as a protonic leak of the membrane.

Such a model provides the means to select and test the efficiency of an industrial prototype designed for adaptation to continuous voltage of 10 to 12 volts which are normally available in a chromium plating shop.

A standard chromium plating plant is normally mounted to avoid excessive loss of the precious product used. Nevertheless, recovery and recycling techniques are necessary at the level of the inactive rinse bath or at the chromium plating bath itself.

After analyzing and localyzing the wastes, E.E.D. is applied to the inactive rinse baths and for the recovery of the chromium plating baths.

The application of the electro-electrodialysis for the recovery of chromium is economically interesting and this process combines the respective advantages of electrolysis and electrodialysis and is flexible to use in all of the electrical processes.

ANNEX B - APPENDIX 5

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RECOMMENDATIONS FOR THE INSERTION OF CONTROL TECHNIQUES IN A WORKSHOP

The informations gathered in Annex A show that the losses generated by the activities of metal finishing appear always in the form of a mixture having variable characteristics with respect to the constituency of the components and their concentrations which, in addition, evolue in time. There are, furthermore, numerous incompatibilities between some products, either for safety reasons, or for reasons of treatment effectiveness which should be applied. This is the case, for example, when mixing cyanides and strong acids and strong bases, nickel and cyanides, chromium and copper, etc...

It has also been shown that the standard means of "treating" these effluents was not adequate on the one hand because this solution confirms a loss of raw materials which is often quite substancial and, on the other hand, because these "treatments" signify, in fact, only a conditioning of the pollutants before being thrown out or disposed of and not a destruction.

In order, for the partisans concerned to research and, if possible to apply a positive solution, even a partial one, rather than a negative purification solution, it is proposed below, to establish a group of means which should allow the partisans to insert the best control techniques or valorization into the system of solutions which are particularly adapted to the cases under consideration.

The preparation and drafting of the calculated statement fo the problem is most often quite difficult and long due to the specificities of the metal finishing operation.

These means are essentially of a methodological nature in order, for applications of technical recommendations, to be carefully studied, and, economically speaking, evaluated and compared in suitable conditions.

The recommendations presented will include :

- analytical means in the form of cards recording the informations gathered, classification and presentation of the problem of the waste in question ;
- technical guides for applying control methods :
  - on the general level,
  - on the individual level ;
- technical guides for selecting this techniques ;
- economic comparison and evaluation outline for operation and investment.

There are four recommendations :

RECOMMENDATION N° 1 :

Identification and classification of product losses.

RECOMMENDATION N° 2 :

Assigning concepts of control-purification-valorization to the various identified wastes.

RECOMMENDATION N° 3 :

Solutions recommended for the technological chains listed.

RECOMMENDATION N° 4 :

Evaluation and comparison of control/purification costs.

These recommendations will be applied either by the manufacturer as a means for management and control for small companies, as a means to provide methodology of substance accounting, laboratory, production, maintenance for large companies, or by research companies specialized in solving a waste problem, or providing impact research prior to the installation of a new plant.

B.A.5.1. RECOMMENDATION N° 1

- Identification and evaluation of product losses :
  - type
  - origine
  - determining factors
  - size
- Classification of product losses as a function of the origine :
  - additives
  - substrates
- Classification of product losses as a function of the loss vector :
  - drag out
  - spent baths
  - miscellaneous

The problem presented must be clearly defined, and to do this, precise basic data must be studied relating to :

- the production
- the products used
- the equipment used.

The basic facts will be recorded on cards, 1, 2 and 3.

For illustration, we shall take the example of a chromic passivation station on a cyanided zinc plating chain.

CARD N° 1

- markings,
- type of treatment,
- design,
- production capacity,
- production hours,
- consumption of additives,
- technological processes.

Card N° 1 takes an inventory of extremely important informations for the following research which should be compiled carefully and with precision.

The card records :

- the type and size of the additives applied in the technological chain,
- the type and size of substrates introduced into the technological chain.

CARD N° 2

-series record-

This card provides a description of the technological chain and particularly of :

- the succession of the baths,
- the succession of the operations,
- the types of baths used ,
- the drainage frequency of the spent baths,
- the structure of the rinsings.

This description will provide a first estimate of the product wastes together with the possible mixtures.

CARD N° 3

This card provides an analysis of the operation of each bath of the technological chain.

It should list, for a given bath, all factors determining the various wastes generated by the bath operation :

- drag out wastes
- drainage wastes
- miscellaneous wastes

The value of the drag out will be examined as an experiment by the static rinse technique in which several tests are performed depending to the variety of the slugs treated.

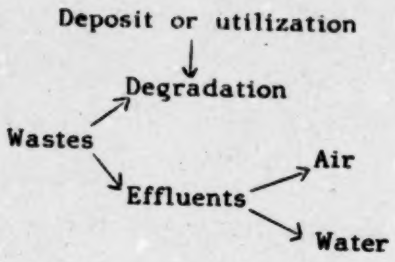
The drag out value will be accompanied by the draining period.

Special attention will be given to secondary treatments which generate , in practice, uncontrolled wastes, the amount of which depends too often on the handler.

The case "volume wastes/day" means the volume lost by evaporation in a 24 hours period, mainly for hot baths.

CARD N° 4

This card provides a substance balance which depicts the various applications of additives based on additives consumed and substrates used,



and to evaluate the various substrate wastes.

NOTE : Wastes from the substrate enter under the same heading as additives which is entitled "consumed products". The difference between these two wastes will already appear on this card N° 4.

CARD N° 5

This card provides for the technological chain studied the various wastes recorded as a function of the technological chain stations, the type and the form of the product wastes.

Cards N° 4 and 5 record the station(s) of the technological chain where control is required after taking into account the type of products and the amount of wastes.

In consideration of the waste vectors and waste origine, guides 6 and 7 make it possible to make an initial evaluation of the possible control or valorization procedures.

APPLICATION OF RECOMMENDATION N° 1

Examination of the various elements relating to the chromic passivation station brings to light that :

- it is a hexavalent chromium waste originating from an additive : chromic anhydride,

- wastes may be broken down into :

. spent baths	1,300 kg/year
. rinsings	200 kg/year

- account taken of the quantities utilized, the study will cover wastes generated by spent baths,

- accordingly, the possible control techniques are theoretically :

. Ion exchangers
. Electrolysis
. Electrodialysis.

CARD N° 1

WORKING HOURS	**HOURS/DAY**	**DAYS/WK**	**HRS/YR**
PRODUCTION	slug type	Basic metal	shape
	Screw.	steel	spiral -
CAPACITY	m2/hr or kg/hr	Av. surf. loaded in kg/drum or dm/hr	
		80 kg/drum	10 drum/hr
DESIGN	Manual :		
	Automatic : yes.		
FLUIDS	Raw water	Demin. water	steam
QUANTITIES AND SPONTANEOUS FLOWS	30 m^3/hr	—	—
	Electricity	Air	
		/	

Water Consumption
on the chain :
15 m^3/hr

TOTAL ADDITIVES CONSUMED

excluding constituents of new baths

Period : 1980.

PRODUCTS	kg/year
Zn anodes	9,000
NaCN	6,000
HCl.	10,000
Degreaser	12,000
CrO_3	4,500
NaOH	3,700
Brightener	500
HNO_3 36°B	3,900
Water	35,000 m^3

PASSIVATION - ZINC PLATING	June, 1980
CHAIN RECORD	SMITH COMPANY

CARD N° 2

STATION	NAME	VOLUME	CONSTITUENCY	DRAINAGE FREQUENCY	
1	Degreasing	2,000 L	salinity 100 g/L.	1/2 wk.	
2	Rinse		Flow 3.75 m^3/hr.		
3.	Rinse				
4	Pickling	2,000 L.	Hcl. 50% (vol.).	once a month	
5	Rinse		Flow 3.75 m^3/hc		
6	Rinse				
7	Zinc Plating	13,000 L.	Zn 40 g/L. Na Cn 110 g/L. Na OH 90 g/L		tank to tank once a year.
8	Rinse		Flow 3.75 m^3/hr.		
9	Rinse				
10	Neutralization	800 L.	HNO_3 0.5% (vol.)	once a day	
11	chrom. passiv.	1,000 L			
12	Rinse		Flow 3.75 m^3/hr.	1/2 days	
13	Rinse				
14	Hot rinse				

ZINC PLATING - PASSIVATION.	June, 1980.
SERIES RECORD	

COMPOSITION OF BATH IN OPERATION			ANNUAL CONSUMPTION 19..		
CHEMICALS	NUMBERS	CONCENTRATION (g/l)	for bath constituency	for maintenance additions	TOTAL
CrO_3	14,250	10	2,500	2,000	4,500
HNO_3 for pH 1.5	15,028				
H_2SO_4	7,920				
COMPOSITION OF THE DRAINED BATH					
Cr VI		10			
Zn + Cr III		2.1			
Draining frequency		1/2 days			

DIMENSIONS

L	2
W	1
H	1.3
Tot. V (m^3)	2.6
us. V (m^3)	2.

IMMERSION PERIOD ~~(mn)~~ 40 sec

STRAINING PERIOD (sec) 30

SUCTION

yes ☐ no ☐

flow ☐

steam treat.

separator cleaning

None

Bath temperature Ambient

Losses vol./day ≃ 0

ANNEX TREATMENTS

FILTRATION PREPARATION TANK

Volume filtred ☐

cleaning frequency ☐

Effluent volume per cleaning ☐

Concentrate volume per cleaning ☐

TANK TO TANK

Volume reserved 15 m³

Treatment frequency 1/yr

Effluent volume per treatment 3 m³

Concentrate volume per treatment 1 m³

HEAT EXCHANGER

Cooling ☐

Heating ☐

Fluide ☐

RECTIFIERS :

Power ☐

Cooling method ☐

DRAG OUT

per bar ______

per drum 1 l.

hourly 10 l/hr

annually 20 m³/year

Tank N° 11

Function Passivation

chemical ☒

cathodic ☐

anodic ☐

catho-anod ☐

CHAIN Zinc Plating

SHOP ______

July, 1980.

CARD N° 3

PRODUCTS CONSUMED	CONSUMPTION kg/year 1980	Spent bath drainage				Running rinse				Misc. losses	steam	deposit	TOTAL LOSSES	LOSSES COEFF.
		vol m3	vol m^3/yr	weight kg/yr		Flow	weight kg/yr							
Na cN	6,000						4,400			110 kg		0	4,510	0,75
Na OH	3,700					3.75 m3/hr	3,600			90kg		0	3,690	0,99
Zinc	9,000						1,600			40 kg		7 360	1,640	0,18
Chromium VI	2,340	1	130	1300		3.75 m3/hr	200					840	1,500	0,55
Degraisser	12,000	2	44	2200			3,000					6 800	5,200	0,43

ZINC PLATING - PASSIVATION

BALANCE CARD

June, 1980

CARD N° 4

STATION	LOSSES IN kg / yr															
	Na CN		Na OH		Zn		Cr VI		Degreaser							
	DL	CL	DL	CL	DL	CL	DL	CL	DL	CL	DL	CL	DL	CL	DL	CL
Zinc Plating	110	4,400	90	3,600	40	1,600										
Passivation							1,300	200								
Degreasing									2,200	3,000						
Iron (substrate)																
SUB TOTALS	110	4,400	90	3,600	40	1,600	1,300	200	2,200	3,000						
GRAND TOTAL	4,510		3,690		1,640		1,500		5,200							

DL : discontinuous losses
Cl : continuous losses

LOSSES DISTRIBUTION CARD	SMITH Company	June, 1980	CARD N° 5

GUIDE N° 6

APPLICATION OF CONTROL TECHNIQUES AS A FUNCTION OF WASTE VECTORS

	DRAG OUT WASTES A	BATH DRAINAGE WASTES B	MISCELLANEOUS WASTES C
Straining	yes	no	no
ECO Rinse	yes	no	no
Static Recovery Rinse	yes	no	no
Ion Exchangers	yes	yes	no
Electrolysis	yes	yes	no
Electrodialysis	yes	yes	no
Evaporation	yes	no	no
Miscellaneous	yes Drag out air	yes	yes operation

GUIDE N° 7

	WASTES FROM ADDITIVES	WASTES FROM SUBSTRATES
Straining	yes	no
ECO Rinse	yes	no
Static Recovery Rinse	yes	no
Ion Exchangers	yes	valorization
Electrolysis	yes	valorization
Electrodialysis	yes	valorization
Evaporation	yes	no
Miscellaneous	yes air suction	no

APPLICATION OF CONTROL TECHNIQUES
AS A FUNCTION OF WASTE ORIGINE

B.A.5.2. RECOMMENDATION N° 2

- Determination of control objectives
- Assigning concepts of
  - control
  - valorization
  - purification,

to the various identified wastes.

Recommendation N° 1 identifies the wastes and makes a first theoretical approximation of the possible control procedures.

Definition of the control objectives results from the above and guide N° 8 provides a definition of the objectives by specifying for the wastes of a given station and for each component the possibilities of control, first, of recovery, next and of purification when the other concepts will be applicable.

APPLICATION OF RECOMMENDATION N° 2

The operation of guide N° 8 confirms the control possibility of bath wastes and that purification is required for the other wastes, particularly for drag out wastes in the case under study.

STATION	MAIN COMPONENTS	DRAG OUT WASTES	BATH DRAINAGE WASTES	MISCELLANEOUS WASTES
CYANIDED COPPER PLATING	copper	control (or valorization)	0	control and purification
	cyanide	control (or purification)		
ACID COPPER PLATING	copper	control (or valorization)	0	control and purification
	H_2SO_4	control (or purification)		
NICKEL PLATING	nickel	control	0	control and purification
DECORATIVE CHROMIUM PLATING	CrO_3	control	0	control and purification
THICK CHROMIUM PLATING	CrO_3	control	0	control and purification
CYANIDED ZINC PLATING OR ACID ZINC PLATING	Zinc	control (or valorization)	0	control and purification
	cyanide	control (or purification)		
CYANIDED CADMIUM PLATING	cadmium	control (or valorization)	0	control and purification
	cyanide	control (or purification)		
CHROMIC PASSIVATION	CrO_3	purification	control	purification
COPPER PICKLING	copper	valorization - purification	valorization	valorization or purification
	H_2SO_4	purification or control	control	purification
STEEL PICKLING	iron	valorization or purification	valorization	valorization or purification
	HCL or H_2SO_4	control or purification	control	purification or control

ASSIGNING THE CONCEPTS OF CONTROL - VALORIZATION - PURIFICATION
TO THE VARIOUS IDENTIFIED WASTES

B.A.5.3. RECOMMENDATION N° 3

Solutions recommended for the technological chains listed

Guides 9, 10, 11 show the various possibilities of applying the control techniques to the case studies.

Guide N° 9 shows these possibilities and it may be observed that for any given case there are several possible technologies due to the fact that these techniques :

- may be induced,
- may be cumulated.

It may be observed that only the control technique by straining may be applied to all the cases studied.

Guide N° 10 shows the interrelations between the various techniques, i.e. the techniques which are necessarily induced by the application of another one. The arrows show the induction direction.

In the case of decorative chromium, for example, the application of electrodialysis on a static rinse induces a second control technique : evaporation to concentrate the chromic acid issued from the electrodialyser and to enable its reintroduction into the chromic plating bath.

Again in the case of decorative chromium, the use of an evaporator induces cascade static rinses and purification of the CrO_3 solution on ion exchangers.

Guide N° 11 shows the various possibilities of cumulating control techniques, case by case.

An evaluation of the yields of the various control systems is regarded.

APPLICATION OF RECOMMENDATION N° 3

Guide N° 9 shows that straining and ion exchangers may be applied for control of losses generated by waste baths from chronic passivation.

Guide N° 10 shows that a second control technique is not induced.

Guide N° 11 brings to light the possibility of cumulating straining/ion exchangers/miscellaneous.

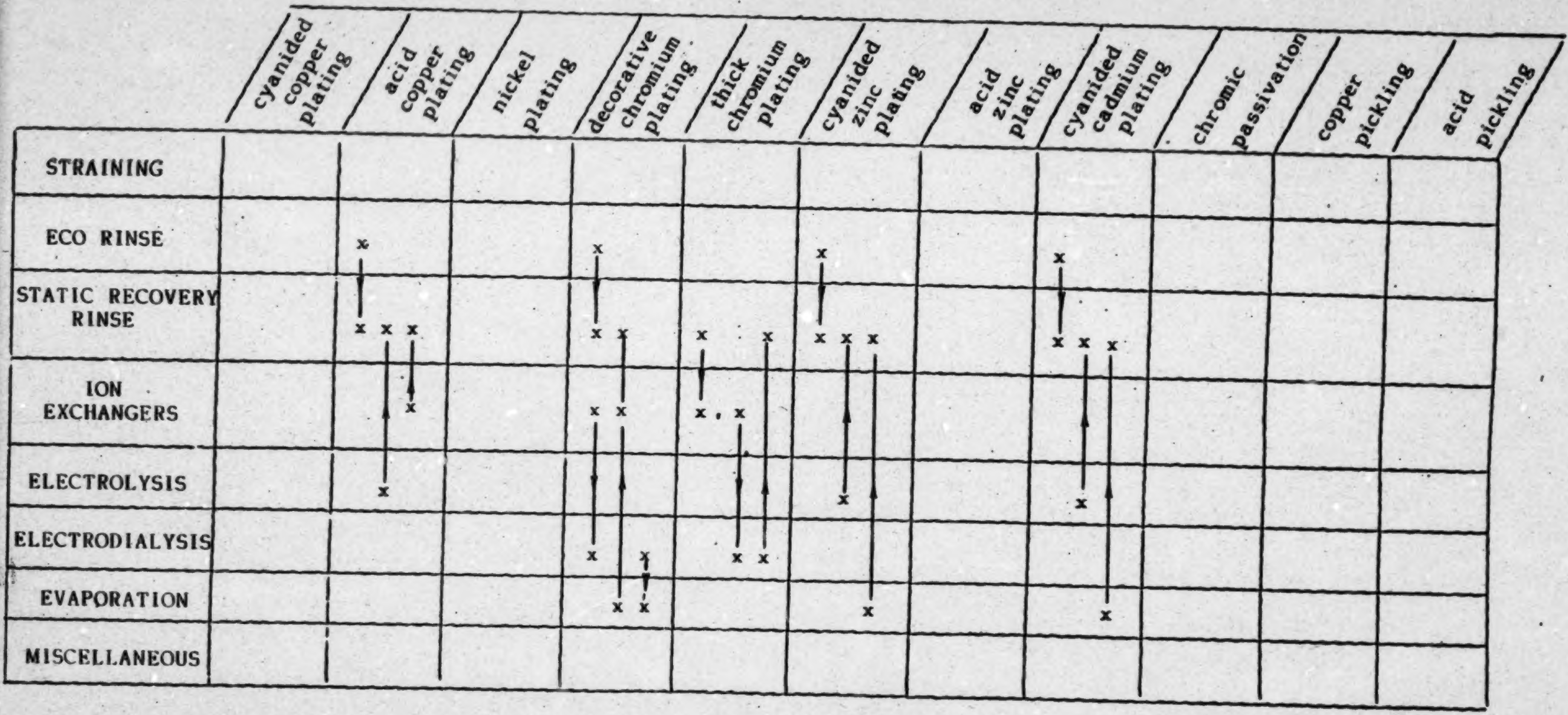
POSSIBILITIES OF APPLYING THE CONTROL TECHNIQUES TO THE CASES STUDIED

ooooooooooooooooooooooo

	cyanided copper plating	acid copper plating	nickel plating	decorative chromium plating	thick chromium plating	cyanided zinc plating	acid zinc plating	cyanided cadmium plating	chromic passivation	copper pickling	acid pickling
STRAINING	X	X	X	X	X	X	X	X	X	X	X
ECO RINSE		X		X		X	X	X		X	X
STATIC RECOVERY RINSE	X		X	X	X					X	X
ION EXCHANGERS		X		X	X				X	X v	X v
ELECTROLYSIS	X	X				X	X	X		X v	
ELECTRODIALYSIS				X	X		X				X v
EVAPORATION				X	X	X		X			
MISCELLANEOUS				X	X				X		

v = valorization

INTERRELATIONSHIPS BETWEEN THE VARIOUS CONTROL TECHNIQUES DEPENDING ON THE APPLICATION


cyanided copper plating
acid copper plating
nickel plating
decorative chromium plating
thick chromium plating
cyanided zinc plating
acid zinc plating
cyanided cadmium plating
chromic passivation
copper pickling
acid pickling
STRAINING
ECO RINSE
STATIC RECOVERY RINSE
ION EXCHANGERS
ELECTROLYSIS
ELECTRODIALYSIS
EVAPORATION
MISCELLANEOUS

v = valorization

POSSIBILITIES OF ACCUMULATING CONTROL TECHNIQUES

	cyanided copper plating	acid copper plating		nickel plating	decorative chromium plating			thick chromium plating		cyanided zinc plating			acid zinc plating		cyanided cadmium plating			chromic passivation	copper pickling	acid pickling	
STRAINING	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
ECO RINSE		X	X		X	X	X			X	X	X	X	X	X	X	X		X	X	X
STATIC RECOVERY RINSE	X	X	X	X	X	X	X	X	X	X	X	X			X	X	X		X	X	X
ION EXCHANGERS			X		X	X		X										X	X	X	
ELECTROLYSIS		X	X								X		X			X			X		
ELECTRODIALYSIS						X			X					X							X
EVAPORATION					X	X						X					X				
MISCELLANEOUS					X	X	X	X	X									X			
CONTROL EFFICIENCY	98%	80%	98%	98%	98 %	98 %	70 %	95%	95%	70 %	80 %	98 %	80%	80%	70 %	80 %	98 %	98%	98%		

B.A.5.4. RECOMMENDATION N° 4

Cost Evaluation And Comparison

This recommendation comprises three parts :

- Operating expenditures,
- Investment expenditures :
  - A- Metal finishing shop
  - B- Control provisions
  - C- Purification provisions
- Summary.

These documents permit the following recapitulations to be compared after operation :

1. Annual cost of an operation without control provision, i.e. :
   - disposal,
   - purification.
2. Annual cost of an operation with control provision, i.e. :
   - control,
   - purification.

OPERATING EXPENDITURES	Consumption	Cost/unit	TOTAL	Annual Cost
WATER				
~~Rinses~~				
Draining and bath maintenance	2 000 m^3			
Purification				
Control		2 F./m^3	4 000 F.	
~~Other~~				
Taxes-and licence fees				
				4 000 F.
PRODUCTS				
Additives CrO_3	4.5 T	8 000 F./T	36 000 F.	
Purification products per kg CrO_3		10 F.	28 000 F.	
~~Control products~~				
Fees	2 000 eq./T	1 F./eq	9 000 F.	
				73 000 F.
ENERGY				
~~Metal finishing~~				
~~Control provision~~				
Purification 8 kWhr x 1,250 hr	10,000 kWh	0.25 F/kWh	2,500 F.	2,500 F.

PERSONNEL				
Operation 0.5 hr per day	120 h	50 F./h	6 000 F.	
				6 000 F.
MAINTENANCE				
Labour Equipment } Reserve			3 000 F.	
				3 000 F.
OUTSIDE SERVICES				
~~Subcontracting~~				
Sludges 60 m^3		20 F./m^3	1 200 F.	
~~Other transfers~~				
~~Technical aid~~				
				1 200 F.
FINANCIAL AIDS				
MISCELLANEOUS				
				89,700 F.

INVESTMENT EXPENDITURES		EQUIPMENT	LABOUR	TOTAL INVESTMENTS	ANNUITIES
Ⓐ METAL FINISHING SHOP MODIFICATIONS					
1 Tanks and direct equipment	supports				
	grating				
2 Hydraulic supply and collection					
	valves				
	piping				
	miscellaneous				
3 Handling methods					
	carriers				
	rail				
	supports				
	drums				
4 Electrical equipment					
	automatism				
	low voltage				
	continuous				
	alternating				
	cable system				
5 Civil Engineering	plant floor (m^2)				
	preparation				
	slabs-sump				
	low wells supports				
	miscellaneous				
6 Anti-acid coatings					

INVESTMENT EXPENDITURES		EQUIPMENT	LABOUR	TOTAL INVESTMENTS	ANNUITIES
Ⓑ CONTROL PROVISIONS					
7	Equipment				
8	Connections - hydraulic - electric				
9	Civil engineering Preparation - drainage Slabs - sump - low walls plant floor m2				
10	Anti-acid coatings				

INVESTMENT EXPENDITURES	EQUIPMENT	LABOUR	TOTAL INVESTMENTS	ANNUITIES
ⓒ PURIFICATION PROVISIONS				
11 Equipment electrical electromechanical reactors storage regulation-control ~~ion exchangers~~	150,000 F.	30,000 F.	180,000 F.	
12 Civil engineering gutters or communication galleries plant basement (m2) heating-lighting-access	40 m^2 at 1,500 F.		60,000 F.	
13 Effluent collection - piping 14 Iron work and miscellaneous			5,000 F.	
15 Anti-acid coating	40 m^2 at 150 F.		6,000 F.	
			251,000 F.	50,000 F.
Ⓓ FINANCIAL AID Example : conditional subsidy of 50 %			125,500 F.	25,000 F.

SUMMARY

ANNUAL OPERATING EXPENDITURES.................		89,700 F.
INVESTMENT EXPENDITURES..	125,000 F.	
ANNUITY............		25,000 F.
TOTAL COST/YEAR..		114,700 F.

OPERATING EXPENDITURES		Consumption	Cost/unit	TOTAL	Annual Cost
WATER					
	~~Rinses~~				
	~~Draining and bath maintenance~~				
	Purification	300 m^3	2 F./m^3	600 F.	
	Control				
	~~Other~~				
	Taxes and licence fees				600 F.
PRODUCTS					
	Additives CrO_3	2 T	8 000 F./T	16,000 F.	
	Purification products per kg CrO_3			8,000 F.	
	Control products				
	Fees	2,000 F.	1 F./eq	4,000 F.	28,000 F.
ENERGY					
	~~Metal finishing~~				
	Control provision	18,000 kWh	0,25 F./kWh	5,750 F.	
	Purification 8 kWhr x 1,250 hr	5,000 kWh			5,750 F.

PERSONNEL				
Operation 0.75 hr per day	180 h	50 F./h	9,000 F.	
				9,000 F.
MAINTENANCE				
Labour				
Equipment Reserve			3,000 F.	
				3,000 F.
OUTSIDE SERVICES				
Subcontracting				
Sludges 20 m^3		20 F./m^3	400 F.	
Other transfers				
Technical aid				
				400 F.
FINANCIAL AIDS				
MISCELLANEOUS				
				46,750 F.

INVESTMENT EXPENDITURES		EQUIPMENT	LABOUR	TOTAL INVESTMENTS	ANNUITIES
Ⓐ METAL FINISHING SHOP MODIFICATIONS					
1 Tanks and direct equipment	supports grating				
2 Hydraulic supply and collection	valves piping miscellaneous				
3 Handling methods	carriers rail supports drums				
4 Electrical equipment	automatism low voltage continuous alternating cable system				
5 Civil Engineering	plant floor (m^2) preparation slabs-sump low wells supports miscellaneous				
6 Anti-acid coatings					

INVESTMENT EXPENDITURES		EQUIPMENT	LABOUR	TOTAL INVESTMENTS	ANNUITIES
Ⓑ CONTROL PROVISIONS					
7	Equipment			90,000 F.	
8	Connections - hydraulic - electric			15,000 F.	
9	Civil engineering Preparation - drainage Slabs - sump - low walls plant floor m2	20 m^2 at 1,500 F		30,000 F.	
10	Anti-acid coatings	20 m^2 at 150 F		3,000 F.	
				138,000 F.	27,600 F.

INVESTMENT EXPENDITURES	EQUIPMENT	LABOUR	TOTAL INVESTMENTS	ANNUITIES
Ⓒ **PURIFICATION PROVISIONS**				
11 Equipment electrical electromechanical reactors storage regulation–control ~~ion exchangers~~	100,000 F.	20,000 F.	120,000 F.	
12 Civil engineering gutters or communication galleries plant basement (m2) heating–lighting–access	25 m^2 at 1 500 F.	-	37,500 F.	
13 Effluent collection – piping 14 Iron work and miscellaneous			5,000 F.	
15 Anti-acid coating	25 m^2 at 150 F.		3,750 F.	
			166,250 F.	
Ⓓ **FINANCIAL AID** Example : conditional subsidy of 50 %			$\boxed{83,125 \text{ F.}}$	$\boxed{16,625 \text{ F.}}$

S U M M A R Y

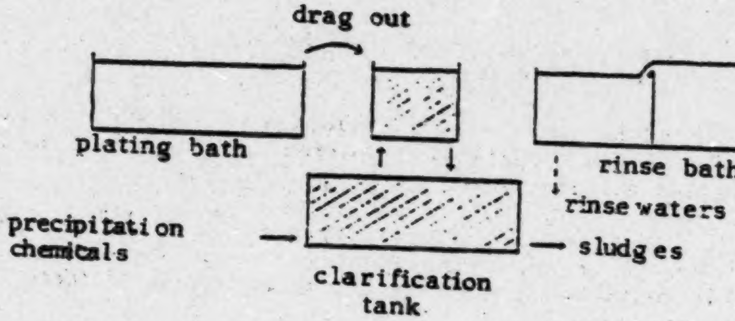
ANNUAL OPERATING EXPENDITURES.................	46,750 F.
INVESTMENT EXPENDITURES..	221,125 F.
ANNUITY............	44,225 F.
TOTAL COST/YEAR..	90,975 F.

ANNEX C

TREATMENTS OF EFFLUENTS

C.1. TREATMENT INTEGRATED IN THE TECHNOLOGICAL CHAIN

The integrated process treats the drag out of the plating bath at the source and permits metals to be extracted from it in the form of sludge. The first rinse bath is replaced by a bath flow inducing the chemical precipitation of metals. The flux containing precipitation chemicals and drag out of the plating bath are collected in a tank where the precipitate is stabilized and the sludge is deposited. The clarification bath may be used on several plating chains, provided that they use the same metal.



This process is widely used, especially for chromium, copper cyanide and nickel sulphate and allows their recovery when the sludges produced contain only one metal.

This treatment is economical and has a simple technology and may be used in small plants.

C.1.1. Kastone Process

A hydrogen peroxide and formaldehyde based oxidizing mixture in static rinse baths permits the oxidation of cyanides into cyanates and the precipitation of metals in the form of oxides rather than in hydroxides. This treatment may be applied after a cadmium plating or a cyanided zinc plating. The precipitates are filtered. The filtrate still contains cyanates, ammonia and an organic acid which may increase the DBO5 of the effluents.

The toxicity of the sludges is distinctly lower after applying this process and the zinc and cadmium oxides are less soluble than the corresponding hydroxides and may therefore be recovered and valorized.

This process is competitive with other purification techniques and is widely marketed.

C.1.2. Lancy Process (chromic acid treatment)

After static recovery rinses, one or two rinses are connected with :

- a station of hexavalent chromium reduction,
- a station of trivalent chromium precipitation.

C.1.3. Nickel

Applying integrated treatment on nickel plating chains in large shops favours recovery:.

Nickel sulphate is removed with sodium bicarbonate, then precipitated nickel carbonate is dewatered and removed into pure nickel carbonate which may be added to the plating bath.

This technique is widely used when a direct recycling of rinse waters is prohibited because of a rapid degradation of organic additives. It could be applied on any other metals if their cost increases any longer.

Nickel recovery rate is about 95 %. But a well studyed rinsing will often be preferable.

C.2. CYANIDE REMOVAL

C.2.1. Oxidation by hypochlorites : ClO^-

This is the most commonly used process for an individual treatment of cyanided effluents, at least its first step. It is especially recommended when the raw effluent contains from 100 mg CN^-/l to 1 g CN^-/l. Cyanided complexes are not satisfactorily destroyed with this process.

Medium investment may be evaluated to 180,000 FF for a 10 m^3/hr flow and the operation cost price is 3 FF/m^3 when oxydizing into cyanate a 100 mg CN^-/l solution, and 4,5 FF/m3 when degradizing it into $CO_2 + N_2$.

a) Oxidation of CN^- into CNO^-

$$CN^- + ClO^- \longrightarrow CNO^- + Cl^- \text{ at pH} > 11$$

b) Hydrolysis of CNO^- in neutral medium

$$2CNO^- + 3ClO^- + H_2O \longrightarrow 2CO_2 + 2OH^- + N_2 + 3Cl^-$$

. By scrupulously respecting the pH an rH zones through adding reactives in controlled amounts, it is possible to obtain the formation of non toxic products (carbon dioxide and nitrogen) ;

. It is indispensable to add an excess amount of hypochlorite (10 to 15 % more than the stoechiometric amount) to ensure a complete destruction of the cyanides, as secondary reactions neutralize part of the reactive ;

. In spite of all precautions, it is possible to prevent a moderate CNCl formation only if there is an excess amount of oxidant together with a very high pH ;

. The reaction yield and its speed are function of pH ;

. Cyanogen chloride, CNCl, fatal in small doses, may be released if the temperature exceeds 40° C. As the oxidation reaction is exothermic, the pollution rate must be controlled (CN^- content of waters to be treated). This is why this process is reserved for spent waters and effluents which do not contain more than 1 g/l of CN ;

. pH of the solution to be treated is brought by adding soda, and it shall be therefore more economical to treat solutions containing high CN^- concentrations ;

. According to the reaction stoichiometry, it follows that for 100 grams of NaCN, 375 grams of hypochlorite are needed, which corresponds to 180 grams of chlorine.

In practice, it is necessary to work with excess amounts due to secondary reactions. Accordingly, 22 to 25 liters of hypochlorite (marked with 15 % activated chlorine) at 50° chlorometric per kilogram of NaCN to be treated ; i.e. 50 liters per kilo of CN^-.

C.2.2. By gazeous chlorine Cl_2

The reactions of oxidation are the same as with hypochlorites. The weakened chlorine is guided through a chlorometer to be solved in water.

. The chlorine water thus obtained must be neutralized, then alkalinized and the amount of soda consumed shall be greater than with the method using hypochlorite ;

. In general, it is assumed that 3 kg of gazeous chlorine are required to reach the cyanate phase, and 7.5 kg are required to reach the nitrogen and carbon dioxide phase per kg of cyanide expressed in CN^-. 3.5 kg of soda must be added to alkalinize each cubic meter of chlorine water.

C.2.3. By persulphuric acid : H_2SO_5

This process destroys cyanided complexes and may be used for concentrations of CN^- up to 5 g/l, but it is specially recommended for contents lower than 100 mg/l. Residual content is lower than 1 mg/l of CN^-.

The investment is lower than for hypochlorites (an average of 150,000 FF for 10 m^3/hr) but operation costs are higher (6 FF/m^3 to oxidize into cyanates a solution of 100 mg CN/l and 11 FF/m^3 for its degradation into $CO_2 + N_2$)

. Oxidation of CN^- into CNO^-

$$CN^- + H_2SO_5 \rightarrow CNO^- + H_2SO_4 \text{ at pH} > 9$$

. Hydrolysis of CNO^-

$$2CNO^- + 3H_2SO_5 \rightarrow N_2 + 2CO_2 + 2H_2SO_4 + H_2O + SO_4{=}$$

. About 30 kg persulphuric acid at 20 % are required to oxidize 1 kg of CN^-. Adding soda may be necessary to maintain pH at 9 and to prevent the risk of releasing hydrocyanic acid ;

. Considering its cost price, persulphuric acid will be used rather for effluents already oxidized by any other (more economical) method in order to oxidize residual cyanides ;

. $KHSO_5$ may be used instead of H_2SO_5. In this case, oxidizing 1 kg CN^- requires 29 kg $KHSO_5$ actived at 40 %.

C.2.4. By perhydrol or hydrogen peroxide : H_2O_2

This treatment is suitable for having a CN^- content below 100 mg/l. An excessive pollution rate would cause hydrocyanic acid to be produced. The residual content is lower than 0.1 mg CN^-/l and cyanided complexes are destroyed. However, hydrogen peroxide is used less often than persulphuric acid although operating costs using perhydrol are lower.

a) oxidation of CN^- into CNO^-

$$CN^- + H_2O_2 \longrightarrow CNO^- + H_2O \quad pH > 9$$

b) hydrolysis of CNO^-

$$2CNO^- + 3\ H_2O_2 \longrightarrow N_2 + 2\ HCO_3^- + 2\ H_2O$$

. pH must be kept at a minimum of 9 otherwise hydrocianic acid would be produced.

. If the effluent ot be treated does not contain copper, it is necessary to add 0.03 to 0.1 g/l of $Cu\ SO_4,\ 5\ H_2O$.

In fact, the reaction of oxidation is very slow if the ion CN^- is combined with the cations of alkaline metals. On the other hand, its speed becomes of interest if the ion CN^- is combined with heavy metal cations like in nickel and particularly in copper ;

. to obtain an oxidation of the cyanides at the cyanate phase, there must be 5 liters of H_2O_2 at 35 % (130 volumes) per kilogram of CN^- and 50 to 100 grams of $CuSO_4,\ 5H_2O$ per m3 of effluent.

The phase $N_2 + CO_2$ may be reach by adding 12.5 l H_2O_2 per kilogram CN^- and 100 g $Cu\ SO_4,\ 5H_2O$ per m3 of effluent.

The reaction lasts about 2 hours and may be controlled at rH meter.

. neutralization costs after oxidation are low due to the low pH.

UGINE KUHLMANN Society filed an application for a patern employing, in fixed pH conditions (10 to 11) both sodium hypochlorite and hydrogen peroxide which leads to very reactive oxygen to be released.

This process allows for a rapid oxidation of every free cyanides and cyanided complex, except for ferro- and ferricyanides, without any pH modification, and for a cost price which should be very low. The reaction would be :

$$H_2O_2 + Na\ ClO \longrightarrow H_2O + NaCl + O_2$$

and :

$$CN^- + \tfrac{1}{2}\ O_2 \longrightarrow CNO^- \quad \text{(cyanates)}$$

H_2O2 is introduced first, in a small excess amount, prior to hypochlorites introduction, to prevent the release of cyanogene chloride.

The oxidant power of such a reactive oxygen would be much higher than the oxidant power of hypochlorites or hydrogen peroxide alone. the raw material cost price would be reduced by 30 % compared with using one of the two oxidants alone.

Because of the high speed of the oxidation reaction by the couple H_2O_2 + Na ClO, the volume of the treatment tanks may be reduced, which has a favourable influence on the investments.

Moreover, the reactive oxygen has other properties : it allows the removal of cyanides without any catalyst : sulphocyanides, phenols, nitrites, sulphides, etc... and an important part of organic matters contained in raw waters.

C.2.5. By ozone : O_3

a) oxidation of CN^- into CNO^-

$$CN^- + O_3 \longrightarrow CNO^- + O_2 \quad \text{at} \quad \text{pH } 11\text{-}12$$

b) hydrolysis of CNO^-

$$2CNO^- + 3O_3 + H_2O \longrightarrow 2\,HCO_3^- + N_2 + 3O_2$$

. The reaction of destruction is rapid, but if the effluents do not contain heavy metals, copper or manganese must be added as catalysts.

. Some cyanided complexes, especially iron and nickel ones, are more stable and resist the combined treatment by ozone and chlorine in an alkaline medium. During the treatment by ozone, irradiation of waters which contain such complexes by U.V. rays of a weak intensity makes complex removal and cyanide oxidation easier.

. Ozone is produced by ozoner where air or oxygen streams flow ;

. 18 kWhr are required to produce 1 kg ozone from air and 9 kWhr from pure oxygen ;

. 1.8 to 2 kg ozone are required to oxidize 1 kg CN^- ;

. An advantage of this process is that there is no discharge of saline products, but buying and maintenance of ozoner are rather expansive.

C.2.6. By persulphates $(NH_4)_2 S_2O_8$ or $Na_2 S_2O_8$

a) Oxidation of CN^- into CNO^-

$$CN^- + SO_8^{--} + H_2O \longrightarrow CNO^- + 2\ H_2SO_4 \quad \text{at pH} > 11$$

b) Hydrolysis of CNO^-

$$2\ CNO^- + 3\ S_2O_8^{=} + 2\ H_2O \longrightarrow N_2 + 2\ CO_2 + 4\ SO_4^{--} + 2\ H_2SO_4$$

. Considering that ammonium ion is present, persulphate is prohibited for the effluents containing metals, for complexes would be produced and they would prevent precipitation from hydroxides when neutralizing.

Hence, this process is reserved for the treatment of regeneration eluates of strong anion resins or of metal free degreasings ;

. 10 to 20 kg $(NH_4)_2 S_2O_8$ are required to oxidize 1 kg CN^-.

C.2.7. By peracetic acid $CH_3 CO_3H$

a) oxidation of CN^- into CNO^-

$$CN^- + CH_3CO_3H \longrightarrow CNO^- + CH_3CO_2H$$

b) hydrolysis of CNO^-

$$2CNO^- + 3CH_3CO_3H + H_2O \longrightarrow N_2 + 2HCO_3^- + 3\ CH_3CO_2H$$

. This acid has the advantage to be biodegradable, but it is not efficient for every cyanided complexes.

. 7.5 liters of peracetic acid (d = 1.100) are required to oxidize 1 kg of CN^- .

C.2.8. By ferrous sulphate : Fe SO4

a) Removal of CN^- into ferrocyanide :

$$Fe^{2+} + 6CN^- \longrightarrow \left[Fe(CN)_6\right]^{4-} \qquad pH : 8 \text{ to } 12$$

b) Precipitation

$$\left[Fe(CN)_6\right]^{4-} + 2Fe^{2+} \rightarrow Fe_2\left[Fe(CN)_6\right] \text{ (prussian white) pH 6.5 to}$$

$$3\left[Fe(CN)_6\right]^{4-} + 4Fe^{3+} \rightarrow Fe_4\left[Fe(CN)_6\right]_3 \text{ (prussian blue) pH 5 to 6}$$

. "Prussian white" is obtained by using pure ferrous salts, without any ferric impurety. "Prussian white" is easy to settle and to filter, in contrast to the "prussian blue".

. "Prussian blue" is able to release hydrocyanic acid by photochemical degradation or when acidified.

. this process is reserved to very concentrated solutions for which oxidation by chlorine or hypochlorite is prohibited (cyanogene chloride could be released because of warming).

. The reaction works too slow to be satisfying in the case of diluted solutions.

. 3 kg of anhydrous ferrous sulphate or 5.5 kg of cristallysed ferrous sulphate are required to treat 1 kg of CN^- . Real consumption is always higher. Sludges are copious.

C.2.9. By catalytic combustion

This process is suitable for the treatment of concentrated cyanided effluents. It is thus recommended for treating spent baths and regeneration eluates. Residual contents from 10 to 50 mg/l of CN^- are obtained, so finishing by persulphuric acid is required. Investment costs and required space make this process reserved to collective centres or any other waste water treatment plant.

Operation costs are about 7 FF/kg CN^- for a solution of 20 g CN^-/l, or 350 FF/m^3.

a) Removal of cyanides

$$2\ CN^- + H_2SO_4 \longrightarrow 2\ HCN + SO_4^{--}$$

b) Combustion. of HCN

$$4\ HCN + 5\ O_2 \longrightarrow 4\ CO_2 + 2\ N_2 + 2\ H_2O$$

. Cyanided concentrates are injected together upon sulphuric acid into the top of an extraction column, into the base of which 1 m3 air per liter of cyanided solution is injected.

- Usual metallic cyanided complexes are entirely destroyed on the extraction column ;

- 99.9 % of the hydrocyanic acid is dragged out by air ;

- Considering the vesicular drag out, the air located with acid is guided through a separator prior to the furnace. The extracted liquid phase is mixed with the decyanided effluent from the base of the extractor and guided to neutralization ;

- The air located with acid is heated to 175° C prior to being introduced into the catalyse furnace ;

- In order to the whole hydrocyanic acid be destroyed, the temperature must be about 300° C at the beginning. The reaction is exothermic, so the temperature reaches 650° C at the end. The heater is supplied with recovered heat.;

- After combustion, gases are sucked up. The furnace operates thus with a low depression ;

- In spite of heat recovery, 1 800 kcal/hr are required for 1 kg CN^-/hr.

C.2.10. By electrolysis of cyanides

By electrolysis, cyanides from 2 to 200 g/l are oxidized into cyanates with a faradic yield not far from 100 %, but the electrolysis is limited by increasing resistance (down to 100 or 500 mg/l).

Finishing with persulphuric acid is thus required as for catalytic combustion.

Economically speaking, there is a little difference between the latter and electrolysis, considering the energy consumption.

C.3. REMOVAL OF HEXAVALENT CHROMIUM

C.3.1. Reduction by sodium bisulphite

This process is suitable for effluents which contain from 20 mg/l to 2 g/l of hexavalent chromium. (For higher contents, chromic acid should be recovered by evaporation or by ion exchange). The residual content is lower than 0.1 mg/l.

The average investment is 180,000 FF for 10 m^3/hr facilities. Operating costs are about 3.5 FF/m^3 for an effluent containing 150 mg Cr/l.

The reaction is the following :

$$4H_2CrO_4 + 6Na\ HSO_3 + 3H_2\ SO_4 \longrightarrow 2\ Cr_2\ (SO_4)_3 + 3\ Na_2\ SO_4 + 10\ H_2O$$

. This reaction is almost instantaneous when the pH is lower than 2.5 and the bisulphite consumption follows the stoechiometric needs. When the pH is higher, the reaction speed decreases very quickly and an excess amount of bisulphite is required.

. When Ca^{2+} or Fe^{3+} are present, the bisulphite consumption may increase ;

. stoechiometric quantities to reduce 1 kg of chromic acid are 1.56 kg of $NaHSO_3$ and 0.74 kg of $H_2\ SO_4$;

. In order to ensure that the pH is lower than 2.5 and only consumes the stoechiometric quantity of bisulphite, an excess amount of sulphuric acid is added ;

. When precipitating, copious sludges are produced. Their weight varies from 4 kg when quick lime is employed, to 1.1 kg when soda is employed, per kilo of chromic acid.

C.3.2. Reduction by sulphur dioxide : SO2

The reaction is :

$$2\ H\ CrO_4 + 3\ SO_2 \longrightarrow Cr_2\ (SO_4)_3 + 2H_2\ O$$

. The reduction technique is similar to using bisulphite. An added acidification is not necessary ;

. The stoechiometric consumption is 0.96 kg of sulphur dioxide per kilo of chromic acid ;

. Sulphur dioxide is injected into residual waters.

C.3.3. Reduction by ferrous sulphate : Fe SO4, $7H_2O$

The main characteristics of the raw effluent and of the treated effluent are the same as for the bisulphite process. Yet, the volume of the sludges produced by using ferrous sulphate is much greater.

The investment is lower than for the bisulphite (an average of 150,000 FF for 10 m3/hr) but operation costs are higher (5.5 FF/m3 for 150 mg/l of Cr).

The reaction is :

$$2H_2CrO_4 + 6FeSO_4 \cdot 7H_2O + 6H_2SO_4 \longrightarrow Cr_2\ (SO_4)_3 + 3Fe_2\ (SO_4)_3 + 15\ H_2O$$

- This method seems to be advantageous, for ferrous sulphate is very cheap, but the reaction works slower than with sodium bisulphite ;

- Stoechiometric quantities are 8.4 kg of cristallysed ferrous sulphate and 2.9 kg of sulphuric acid to reduce 1 kg of chromic acid. In fact, excess amount of sulphuric acid to ensure the pH is lower than 2.5 ;

- 12.4 kg of sludges are produced per kilo of chromic acid when neutralized with soda ; i.e. 3 or 4 times more than using bilulphite ;

- Such an amount of sludges quickly clog any continuous control system. That is why this method has better discontinuous applications.

C.4. FINAL NEUTRALIZATION AND PRECIPITATION OF METALS

Subsequent to the various purifications, it is recommended to mix all residual waters and to adjust the pH between 8 and 8.5 by addition of an alkali or a diluted acid.

This pH area is chosen because most metals precipitate as hydroxides and clear water may be discharged after clarification.

C.4.1. Neutralization

. The neutralization reaction is almost instantaneous and is related to the water ion balance :

$$H^+ + OH^- \rightleftharpoons H_2O$$

Strong acid radicals and some cations stay in solution as ions, without taking part in the reaction.

. Commonly used reactives are :

- acid agents : HCl or H_2SO_4
- alkaline agents : soda, lime, sodium carbonate.

. Sulphuric acid is more economical than hydrochloric acid but content of SO_4^{--} increases in purified waters and putting sulphuric acid in touch with civil engineering concrete is to be avoided. In touch with strong alkaline solutions, sulphuric acid entails a sudden heating.

. Hydrochloric acid is easier to use, but entails a rapid corrosion of all metal preces in the surroundings.

. Soda commonly used as solutions at 450 g/l which make injections easier. But its cost is rather high compared to lime.

. Lime is very cheap but entails very copious sludges. An advantage is that calcium salts have a low solubility. It is widely employed as lime wash. However, added equipment is required which involves a higher investment.

. An advantage of sodium carbonate is the precipitation of some metals (Cd^{++}, Ag^+) at pH 8 instead of pH 9. Cadmium or zinc precipitated basic carbonates have a crystalline structure and are thus easier to clarify and to filter than hydroxides precipated with soda.

. When lime is not used considering the volume of the sludges, but if sulphates, phosphates or fluorides should be eliminated, soda may be employed with the addition of small amounts of soluble calcium salts.

C.4.2. Metal precipitation

It is at maximum for pH between 8 and 8.5

The reactions or metal hydroxide (or carbonate) precipitation consume OH^- ions, therefore the medium pH decreases until all heavy cations are removed to hydroxide. Hence, the pH must be adjusted by adding acid or alkaline agents.

Reaction of precipitation :

$$Fe^{+++} + 6\ H_2O \longrightarrow \left[Fe\ (H_2O)_6\right]^{3+}$$

$$\left[Fe\ (H_2O)_6\right]^{+++} + 3OH^- \longrightarrow Fe\ (OH)_3 + 6H_2O$$

$$\left[Cr\ (H_2O)_6\right]^{+++} + 3OH^- \longrightarrow Cr\ (OH)_3 + 6H_2O$$

$$Zn^{++} + 2\ OH^- \longrightarrow Zn\ (OH)_2$$

$$Cu^{++} + 2\ OH^- \longrightarrow Cu\ (OH)_2$$

$$Ni^{++} + 2\ OH^- \longrightarrow Ni\ (OH)_2$$

. It is not desirable to work at pH higher than 9 for two reasons :

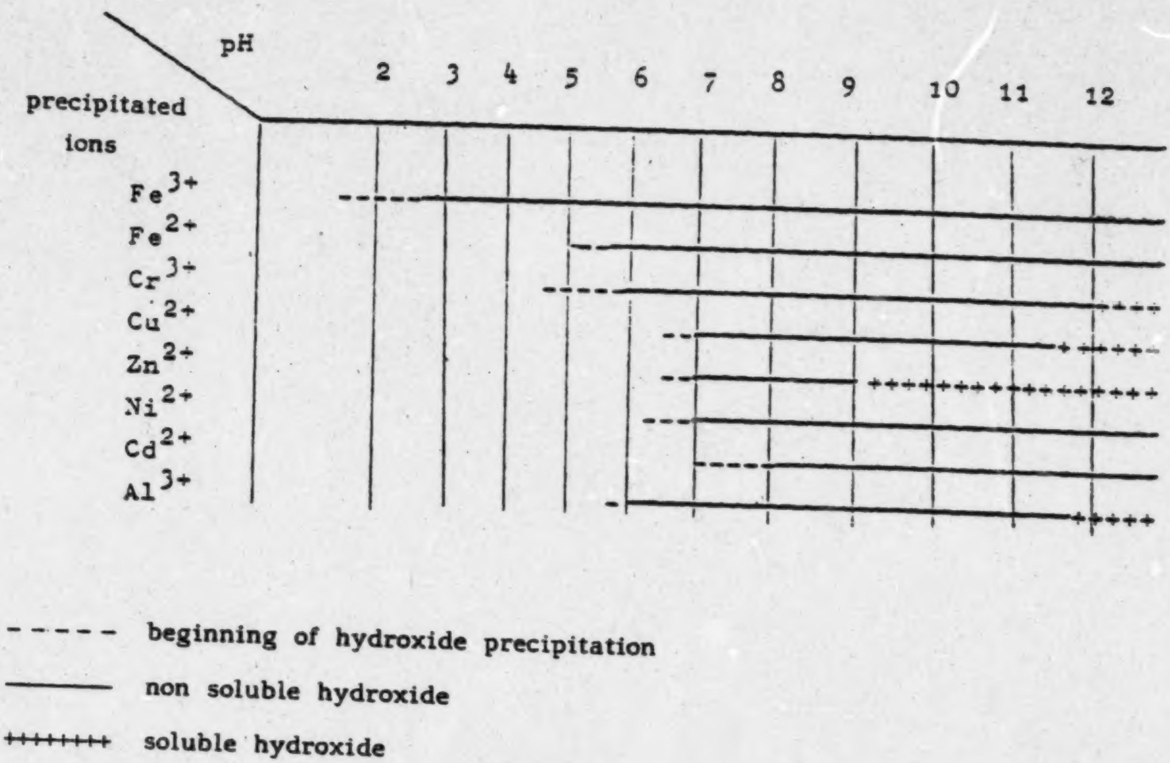
1) proper toxicity of alkaline media

2) some precipitates could be solved

This is the case for zinc and copper hydroxide which solves at pH 9 as toxic ions.

$$Zn\ (OH)_2 + 2\ OH^- \longrightarrow Zn\ (OH)_4^{--}$$

$$Cu\ (OH)_2 + 2\ OH^- \longrightarrow Zn\ (OH)_4^{--}$$



NOTA : Metal sulphides have an aqueous solubility much lower than the related hydroxides. Heavy metals sulphide precipitate easily. The sludge will be denser and easier to dry to 50 % of water by gravity filtration.

C.5. THE CLARIFICATION OF EFFLUENTS

C.5.1. Clarification

Clarification is the seperation of suspended solids, metal hydroxides, and other settleable impurities that are heavier than water by gravitational settling.

Clarification may be achieved in holding tanks which are alternatively supplied, purificated and drained, but this process is only suitable for little facilities on small flows.

The most commonly used clarifiers are :

a) common cylindro-conical clarifiers,

b) static clarifiers with a horizontal flow,

c) static clarifiers with mechanical raking of sludges (cylindro-conical or rectangular in design),

d) speeded clarifiers with sludge beds.

Types c) and d) are reserved for clarifying large volumes of waste waters, therefore high weights of sludges.

In order to make the coagulation easier, flocculents may be added to the waste stream following pH adjustment and prior to gravitational separation. They must be chosen carefully for they can considerably modify the behaviour of sludges when filtered.

Flocculents are of mineral type (iron, aluminium or silicium salts) or of organic type. Polyelectrolytes are synthetical organic flocculents of various polarity.

Anionic and non-ionic flocculents are particularly suitable for mainly mineral sludges whereas cationic flocculents are used for sludges having a high content of colloïdal organic substance.

Flocculation results may be considerably increased by combining various types of polyelectrolytes. A prior test will always be required.

The solid content in the sludges removed from the clarifier depends on the impurities present, the retention time, and the chemical treatment used. It varies from 0.5 to 3 %. Recycling of metal hydroxide sludges back to the clarifier inlet results in densification of the sludges. Moreover, it may be noticed that the presence of old sludges favours the clarification of recently sedimented sludges and that any modification in flows or any temperature gradient entails convection movings which have sludges up to the surface.

An advantage of clarifiers is their efficiency to settle in a short time and a limited area, suspended materials which settle slowly. pH adjustment higher than 9 makes flocculation easier by altering pollutant solubility and often leads to a better effluent quality. A high speed for the flocculation involves a regular maintenance of downstream equipment (filter, pumps...).

C.5.2. Flotation

Flotation is the process of causing particules such as metal hydroxides to float to the surface of a tank where they can be concentrated and removed. This is accomplished by increasing the buoyancy of the solid particles by releasing gas bubbles which attach to the solid particles causing them to float. Flotation may be performed in several ways :

- Froth flotation : air is blown through the solution containing flotation reagents ;
- Dispersed air flotation : gas bubbles are generated by introducing the air by mechanical agitation with impellers or by spraying air through porous media ;
- Dissolved air flotation : bubbles are produced as a result of the release of air from a supersaturated solution ;
- Vacuum flotation : after saturating the waste water with air, a partial vacuum is applied, which causes the disolved air to come out of solution as minute bubbles.

The use of chemicals to improve the efficiency may be employed with any of the basic methods. These are mineral compounds which create a structure that can easily entrap air bubbles, or organic components which change the nature of either the air-liquid interface, or the solid-liquid interface, or both.

The foam is then collected and removed on the liquid surface and treated with caustic soda, soda ash or sodium silicate to break the foam and cause a separation. The separated metals are left concentrated in solution. Laboratory tests showed that metals could be recovered, including hexavalent chromium, and that a prior destruction of cyanides is not required.

Ion flotation is a relatively well developed unit operation in the metal extraction industry, but it is still rarely applied to electroplating waste waters. However, it is more efficient than clarification for wastes that carry finaly divided suspended solids and greases, or solids having a specific gravity only slightly greater than 1.0. Its main disadvantage is that laboratory tests are required prior to each particular case.

C.5.3. Diatomaceous earth filtration

The diatomaceous earth filter is used to remove metal hydroxides and other solids from the waste water and provide an effluent of high quality.

The filter element consists of multiple peat screens which are coated with diatomaceous earth.

The principal advantage to using a diatomaceous earth filter is the reduction in size of the waste treatment system compared to a system using a clarifier. One additional advantage is that the sludge removed from the filter is much drier than that removed from a clarifier (approx. 50 % solids). The investment is lower but the main disadvantage to the use of a filter system is an increase in operation and maintenance costs. However, considering the much higher concentration of sludges, diatomaceous earth filtration is favourable in many cases, especially for the lowest flows.

C.5.4. Mechanical gravity thickening

Mechanical gravity thickener, whose design is similar to cylindro-conical clarifier, may be employed to concentrate sludge prior to dewatering.

Metal finishing sludges, whose solid content is 1 to 2 % after clarification, may be concentrated to 4 or 6 % of dry matter.

C.5.5. Deep bed filtration

Suspended solids are commonly removed from waste water streams by filtering through a deep 0.3 - 0.9 m granular filter bed. The porous bed formed by the granular media can be designed to remove pratically all suspended particles and even colloïdal suspensions (roughly 1 to 100 microns).

The media may be used singularly or in combinations. The multi-media filters may be arranged to maintain relatively distinct layers (multi-layered) by virtue of balancing the forces of gravity, flow, and buoyancy on the individual particles. In actual research, the various media and operating parameters are selected to achieve a natural mixing of the media which yields the relatively continuous variation of bed characteristics desired.

The most common filtration approach is the conventional gravity filter. A variation of the gravity filter is commonly referred to as a pressure filter : filtration works then from the bottom to the top of a steel tank. Other variations are commonly referred to as uniflow, biflow, horizontal flow, and radial flow.

The state-of-the-art in filter technology has progressed during the last years, however, the use of pilot plant filters for a specific application is a necessity as part of the engineering design procedure.

The main advantages of filtration are :

- low initial and operating costs,
- reduced land requirements over other methods to achieve the same level of solids removal,
- no chemical additions which add to the discharge steam.

Some disadvantages encountered with filters are :

- require pretreatment if solid level is high (from 100 to 150 mg/l),
- operator training is fairly high,
- backwash must be stored and dewatered to be economically disposed.

C.6. DEWATERING OF SLUDGES

C.6.1. Filter press

A typical filter press consists of a number of plates or trays which are held together between a fixed and a moving end. On the surface of each individual plate is mounted a filter cloth. The sludge is pumped into the press and passes through feed holes in the trays along the length of the press until the cavities or chamber between the trays are completely filled. The water passes through the fibers of the cloth. A filtration cycle works in four phases : -feeding -filtration -venting and opening-maintenance (which only occurs now and then).

The pressure which may be applied to a sludge for removal of water by filter presses that are now available range from 5 atm to 15 atm. In comparison, a centrifuge may provide forces at 250 atm and a vacuum filter 0.7 atm. As a result of these greater pressures, filter presses offer the following advantages :

- filtration efficiency is improved, especially on materials which are difficult to filter ;
- requirements for chemical pretreatment are frequently reduced ;
- filtrate quality as measured by suspended solids content is improved ;
- maintenance is minimale.

New synthetic fibers have largely offset the short life of filter cloths. Units with automated feeding and pressing cycles are also now available. It is only at the end of the cycle that the process becomes semi-automatic as no foolproof automatic method of discharging the filter cake is yet available.

C.6.2. Sludge bed drying

Sludge bed drying is the process of reducing the water content in a wet substance by spreading the substance on the surface of a sand bed and allowing drainage and evaporation to the atmosphere to dry the sludge. This process is used for the drying of sludge prior to removal to a landfill.

These beds usually consist of 10 to 40 cm of sand (0.5 to 1.5 mm) over a 20 to 30 cm deep gravel drain system made up of 15 to 25 mm graded gravel overlying drain tiles.

Draining results in water concentration as low as 80 % and evaporation allows for a 65 % water content.

Covered drying beds permit a greater volume of sludge drying per year in most climates because of the protection afforded from rain or snow and because of more efficient control of temperature.

The filtration yield can be improved by applying electro-osmosis techniques. The electro-osmotical effects are significant when sludges have a moisture content less than 90 %.

The main advantage of sand drying beds over other types of sludge drying is the relatively low cost of construction, operation, and maintenance.

Its disadvantages are the large area of land required and long drying times that depend, to a great extent, on climate and weather.

ANNEX C - APPENDIX 1

……

NEW TECHNIQUES FOR EFFLUENT TREATMENT

C.A.1. SOLVENT RINSE SYSTEMS

A new rinse -and- recovery system utilizes a combination of countercurrent rinsing, the leading separation techniques and adds a further element of displacement by immiscible fluids. This system uses a two-stages solvent spray rinse followed by a single stage aqueous immersion rinse.

A complete module using perchloroethylene has been managed on a chromium plating bumper line. It shows the technical feasability and the economical interest of this process.

In a U.S. laboratory, a mixture of a high molecular weight amine and xylene was used to extract selectively or simultaneously 90 % of chromium, 98 % of cadmium and 83 % of zinc in a single extraction with an effective ratio waste water to solvent : 100 : 1. The metals were stripped from the organic phase with over 99.5 % efficiency with sodium hydroxide. The regenerated reagent can be recycled and reused without any loss of extraction efficiency. The procedures are reproductible, rapid and relatively simple. Particularly the simultaneous extraction of the three metals shows promise for utilization of small metal finishing facilities.

Solving rinsing is already used in other countries (Sweden, France...).

This system provides complete rinsing in less space, time and cost for a low power consumption. By continuously purifying and recycling the baths, appreciable savings in operating, chemical and waste water treatment costs may be realized.

C.A.2. CEMENTATION

Cementation is the displacement of a metal from solution by a metal higher in the electromotive series.

EPA has completed a full scale study of this technique as a means of removing copper sulphate from plating waste waters.

In this project the waste water was passed over scrap iron and the copper and iron exchanged. The resulting copper could then be recovered as the metal, while the ferrous sulphate was discharged. In the same process, reduction of contaminating hexavalent chromium by scrap iron also takes place, thus eliminating the need for a separate chromium reduction system.

Applications of this process are yet in pilot scale, but the economics seem to be favourable, especially in the case of copper recovery.

C.A.3. ELECTROLYTIC PROCESSES

C.A.3.1. EDF and ANDCO processes : reduction of Cr VI

Voltage is imposed between two consumable iron electrodes. Issued ferrous ions reduce hexavalent chromium according to a reaction similar to ferrous sulphate in alkaline medium (See C.2.3.).

This reaction involves an increase in pH, initially fixed between 7 and 9, of 0.5 to 1 unit which allows for iron and chromium hydroxides precipitation. Initial contents of Cr VI of some 100 mg/l may be decreased to less than 0.05 ppm (for higher contents, chemical processes are more economical).

Moreover, the amount of sludges is half of that produced with bisulphites.

C.A.3.2. Electrolysis on particle beds : cyanide and hexavalent chromium removal

The major part of the cell is a semiconductive polarizable particles bed. When ions touch these numerous micro electrodes, oxidation or reduction reactions take place.

The maximum concentration of the raw effluent is 200 mg/l. Treated effluents have an average chromium content as low as 0.05 mg/l.

Cyanide electrolysis on particle beds requires a chlorination finishing.

Total investment cost is 250,000 FF and operating cost is lower than 25 FF/kg Cr VI for concentrations about 150 mg Cr VI/l.

C.A.3.3. CHEMELEC cells : cyanide removal

When cyanide electro chlorination is integrated in the technological chain, cyanide oxidation works more rapidly especially as free chlorine excess is larger. But heavy metals precipitate immediately, without being able to deposit upon the cathode.

CHEMELEC cells allow for anodic cyanide oxidation and simultaneous deposition of metals upon the cathode. This is possible thanks to a very strong movement of a non-conductive particles fluidized bed lying between two grid electrodes.

Operation costs of this process are much lower than those of conventional chemical processes. There is neither chemical product consumption nor metal sludge generation and metal is recovered with a high degree of purity.

C.A.3.4. Metal recovery from diluted cyanided solutions

A new particle bed system has been developed that concurrently removes metal and oxidizes cyanide. The system employs an electrolytic cell with a cathode bed composed of tin particles, a graphite particle-bed anode and a cellophane separator. Two-stages operation gave overall removal of 95 % of an initial 22 ppm cadmium and 94 % of an initial 44 ppm cyanide. Similar two-stages treatment of zinc rinse waters gave overall removal of 75 % of an initial 57 ppm zinc and 78 % of an initial 195 ppm cyanide.

ECO-CELL features a concentric cathode and anode, separated by a ion exchange membrane and a cavity through which the waste water pass. The cathode rotates inside the cell, while the anode remains stationary. The system is effective for metal loads from 100 to 100,000 ppm and the effluent concentration achievable is in the range of 2.10 ppm. The metal is concentrated as a powder/water mixture and can be recovered.

DU PONT's system aims at more dilute waste streams containing 100 ppm or less of heavy metal. The spiral cell is a sandwich construction containing a fixed stainless steel mesh cathode, a porous separator layer, a screen -like material as the anode and another separator layer.

Typical efficiencies reported are on the order of 90 % for copper. Preliminary economics favour this process versus ion exchange for dilute streams.

C.A.4. CARBON ABSORPTION

Carbon absorption, normally thought of as a means of removing organic pollutants from water, may be used subsequently to preliminary filtration or clarification, for an added purification of metal finishing effluents. Both cyanides and hexavalent chromium are absorbed.

Reactivation is accomplished by heating the carbon to 1 600 - 1 800° F (850 - 1 000° C). Oxygen in the furnace is normally controlled at less than 1 % to effect selective oxidation of contaminants.

The application of activated carbon absorption systems for metal removal is relatively new.

C.A.5. STARCH XANTHATE PRECIPITATION

Heavy metal can be complexed with polymeric polyxanthates such as starch xanthate which acts as an ion exchange resin in the presence of cationic polymers.

The metals are reported to be reclaimable from the starch solid by destruction of the complex with nitric acid or heat. When metal concentrations are higher than 100 mg/l, a pretreatment is required.

Metal sludge settles rapidly and dewaters to 50-90 % solids content after filtration or centrifugation. If the sludge is landfilled, the metal is fairly strongly bound and would have less chance to be leached out than with a hydroxide sludge.

Several electroplaters are investigating full scale use of the process.

C.A.6. OXALATION

Sludges are treated with oxalic acid, then with ammonia, and finally sodium hydroxide. Bivalent copper, nickel and zinc become insoluble oxalates, trivalent chromium and iron are extracted and pH adjusted. The remaining oxalates extract the other metals in the sludge as hydroxides.

This process was developed in Japan and is still in the laboratory research stage.

C.A.7. HIGH pH PRECIPITATION

The treatment of solutions of chelated copper with calcium hydroxide, calcium oxide (lime), calcium chloride or calcium sulphate at a pH of 11.6 - 12.5 will effectively remove copper from the solution as a copper hydroxide.

Flocculation of the copper hydroxide with an anionic polyelectrolyte accelerates the settling of sludge.

This process works well with both concentrated baths and dilute rinse baths. The addition of small amounts of sulphide ions or dithiocarbamates after the calcium ion treatment aids in further removal of copper. The results show the calcium treatment at a high pH to be effective on electroless nickel solutions.

The high pH precipitation process is presently in the laboratory stage of development in the U.S.A.

C.A.8. SULPHIDE PRECIPITATION

C.A.8.1. Sulphide precipitation without any pretreatment of hexavalent chromium

In this process heavy metals are removed as sulphide precipitates. Sulphide is supplied by addition of very slightly soluble metal sulphide which has a solubility somewhat greater than that of the sulphide of the metal to be removed. Normally ferrous sulphide is used.

The process is applicable for the treatment of all heavy metals. It offers a distinct advantage in the treatment of waste water containing hexavalent chromium. The ferrous sulphide acts as a reducing agent at a pH from 8.0 to 9.0 and this reduces the hexavalent chromium and then precipitates it as a hydroxide in one step without pH adjustment. Therefore, hexavalent chromium wastes do not have to be isolated and pretreated by reduction to the trivalent form.

Data on the performance of this process show that concentrations of less than 0.05 mg/l have been achieved for most metals, with levels down to ppb for some sludges are much less subject to leaching than landfilled hydroxide sludges.

C.A.8.2. "Sulfex" process

In "Sulfex" process, the first hydroxide precipitation would be followed by a treatment with sulphide ion to convert residual dissolved metal ions to much more insoluble metal sulphide. Practical constraints such as the low solubility of any usable sulphide ion source precludes hydroxide precipitation could be replaced totally by the sulphide procedure.

The Sulfex process employs a sparingly soluble and non toxic ferrous sulphide as a source of sulphide ion. The principal reactions are as follows :

$$\mathrm{Cu\ EDTA^{2-} + Fe\ S_{(s)} \rightleftharpoons Cu\ S_{(s)} + Fe\ EDTA^{2-}} \qquad (1)$$

$$\mathrm{Fe\ S_{(s)} + 2\ H_2O \rightleftharpoons Fe^{2+} + 2OH^- + H_2S\ (g)} \qquad (2)$$

The first reaction shows that FeS is effective in breaking up complexes and precipitating heavy metals sulphides. The second reaction shows that the FeS-H_2O system is self regulating with respect to the sulphide content of the solution. The amount of H_2S vapor in the air above a saturated FeS solution remains constant regardless of the amount of FeS added.

This constant amount of generated H_2S by the FeS-H_2O system is only 0.003 ppm, which is below the odor detectable level. Thus the use of FeS in the sulfex process offers a significant advantage over the use of soluble sulphide sources (NaHS or Na_2S) which generate hydrogen sulphide by hydrolysis of the excess reagent and require strict control of both pH and reagent addition to avoid odor and safety problems.

The effluent quality depends on the type of complexing agents present, but the process is more effective for a solution of mixed metals rather than a single metal.

Preliminary economics indicate that sulfex should be practical as a polishing treatment following hydroxide precipitation or when the effluent contains up to 50 mg/l dissolved heavy metals. Sulfex is technically feasible and superior to conventional hydroxide precipitation for removal of copper, nickel and zinc. Hexavalent chromium also can be removed by Sulfex in a one-step operation within the pH range of 8 to 9.

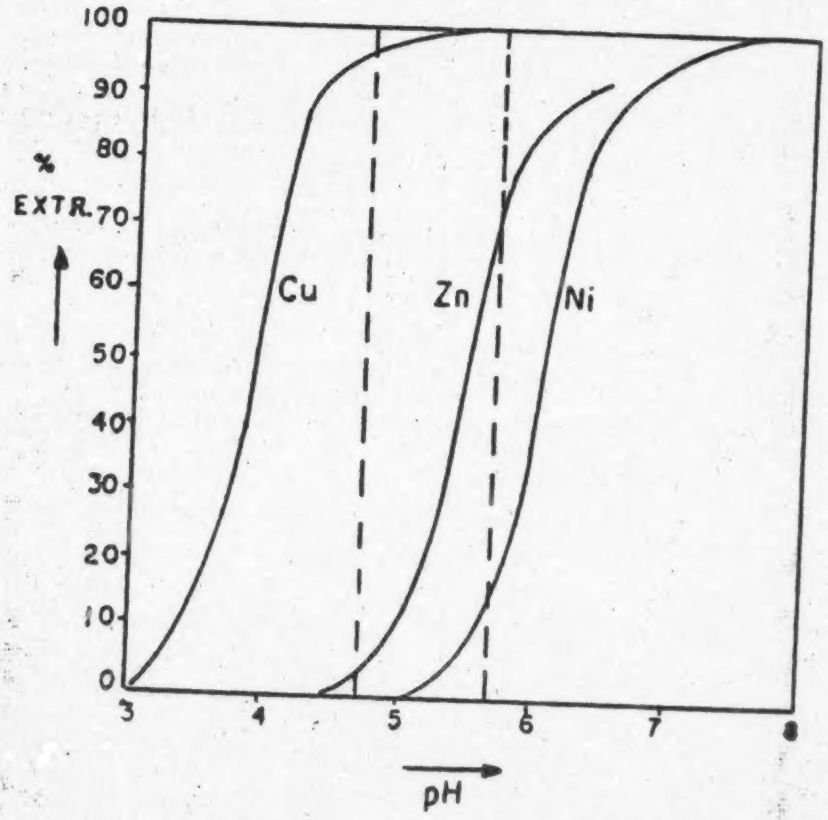
C.A.9. SOLVENT EXTRACTION

The Netherlands investigated in the development of a process allowing for the recovery pure sulphates of Cu, Ni and Zn from metalhydroxide sludges. The process is based on a selective leaching step of the mentioned metals under such conditions that Cu, Ni, Zn, and Cr partly dissolve. Fe remains in the residue. The separation of Cu, Ni and Zn takes place by solvent extraction.

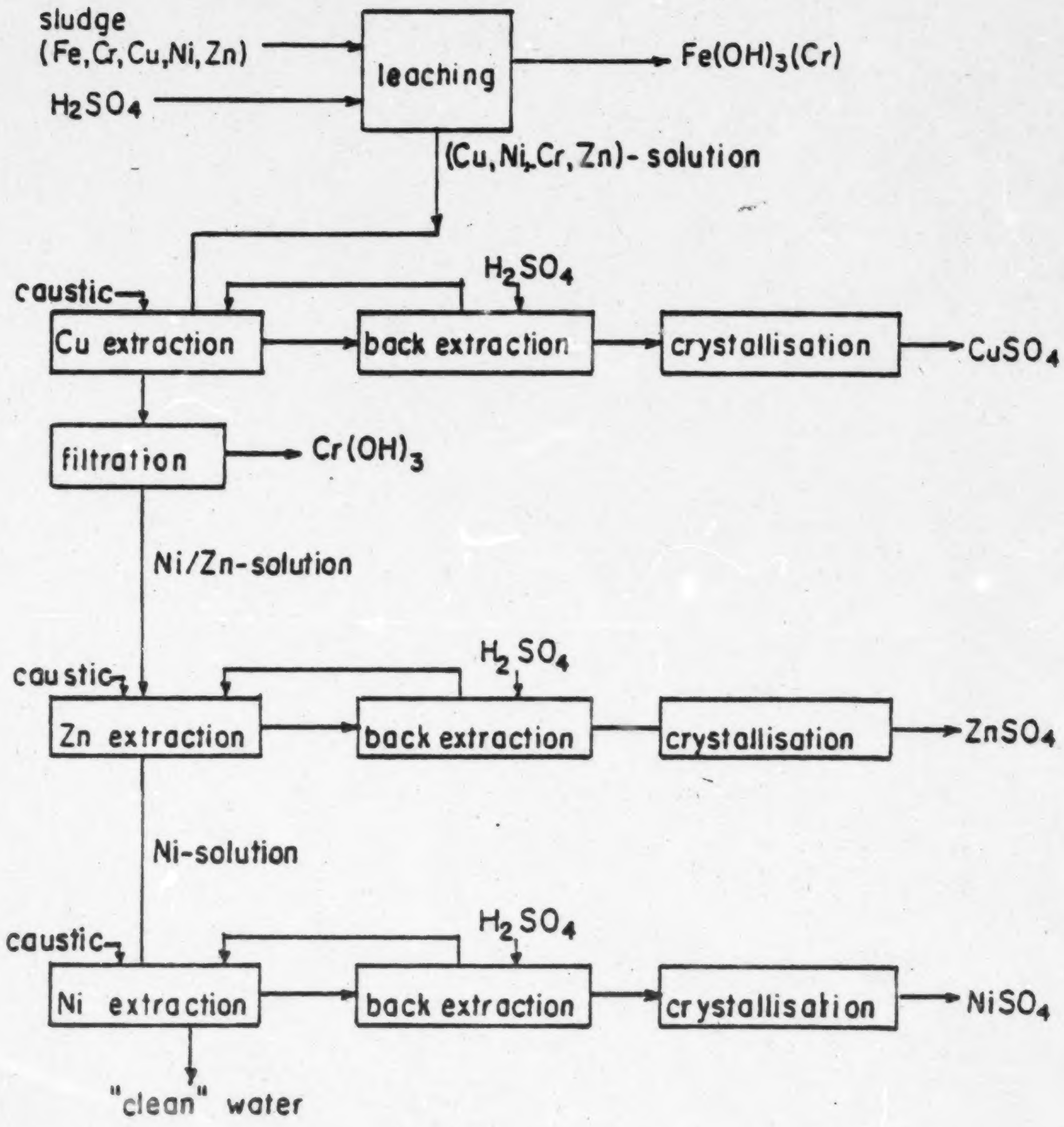
One of the objectives was to develop an appropriate extractant for the separation of these metals. As an alternative to the already existing "LIX-agents" a new agent was developed : a mixture of cyclohex anone oxime and oleic acid. With this agent the separation of the metals takes place as a function of the pH.

SEPARATION OF Cu^{++}, Zn^{++} AND Ni^{++}

DISTRIBUTION CURVES AS FUNCTION OF pH (PHASE RATIO 1:1)



Solvent extraction process


sludge
(Fe, Cr, Cu, Ni, Zn)
H_2SO_4
leaching
$Fe(OH)_3(Cr)$
(Cu, Ni, Cr, Zn)- solution
caustic
H_2SO_4
Cu extraction
back extraction
crystallisation
$CuSO_4$
filtration
$Cr(OH)_3$
Ni/Zn-solution
caustic
H_2SO_4
Zn extraction
back extraction
crystallisation
$ZnSO_4$
Ni-solution
caustic
H_2SO_4
Ni extraction
back extraction
crystallisation
$NiSO_4$
"clean" water

recovery of Cu-, Ni, and Zn- salts from metal hydroxide sludge

The metal sludge is leached with dilute sulphuric acid at pH 3.0.

The leach efficiences, reached on laboratory scale, are : Cr : 65 %, Cu : 95 %, Ni 95 %, Zn : 100 %.

Fe is leached in a small amount : 3 %.

The next process steps consist of successive extractions of Cu^{2+}, Zn^{2+}, and Ni^{2+} at different pH values from the aqueous solution. The respective pH's for Cu^{2+} and Zn^{2+} are 4.7 and 5.7. Cu^{2+} is backextracted from the organic extract. $CuSO_4$ is crystallized with high purity. Pure solid $ZnSO_4$ and $NiSO_4$ are obtained from their respective organic extracts in the same way.

It seems possible to separate Cr^{3+} from the aqueous leachate solution by precipitation as $Cr(OH)_3$ in the course of one of the extraction steps.

Laboratory investigation showed the technical feasibility of the process and the high quality of the metalsalts : $CuSO_4$, $NiSO_4$ and $ZnSO_4$. An important advantage of this process is that only one extractant is needed ; moreover the extractant is cheap.

C.A.10. SELECTIVE ION EXCHANGE

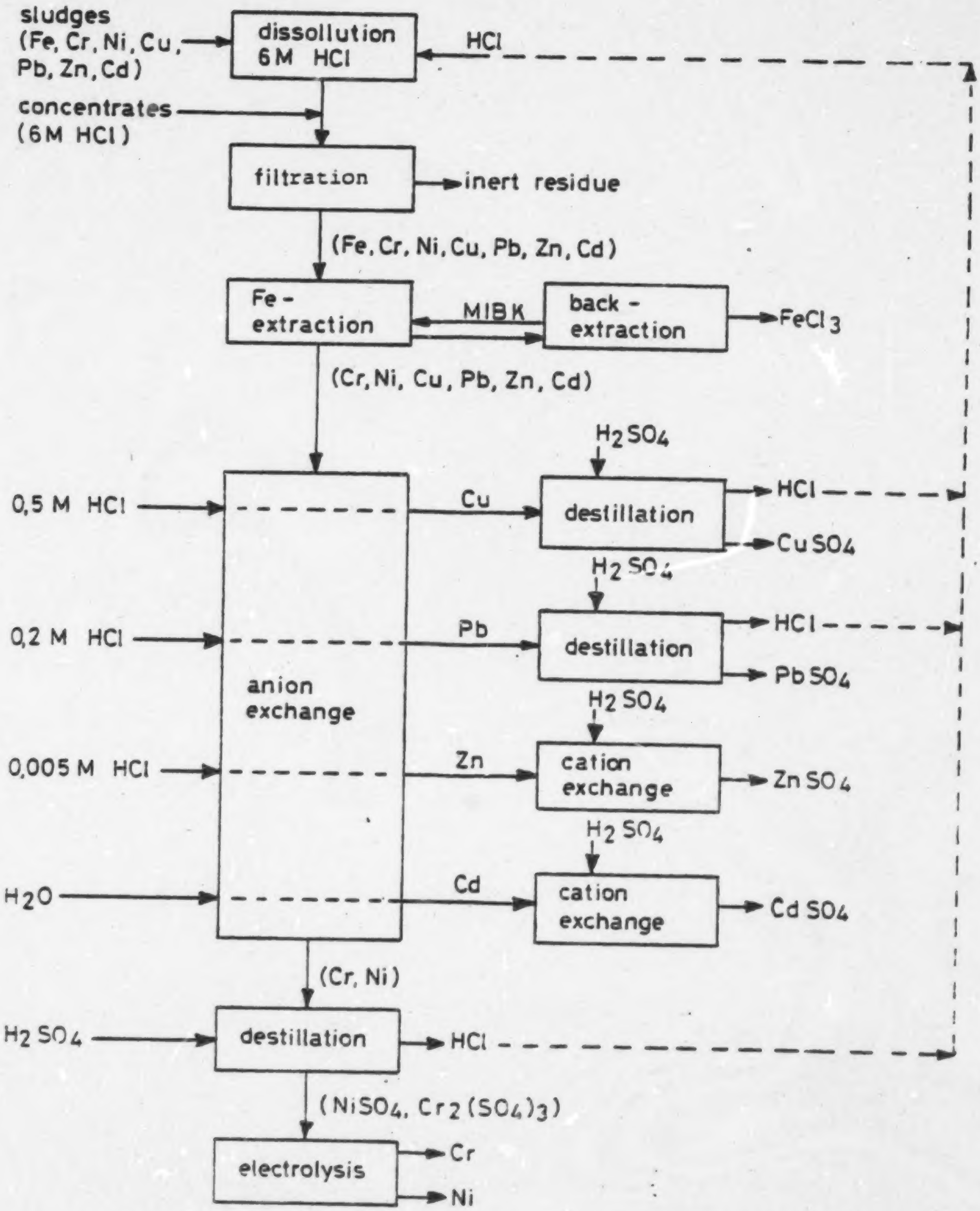
The process developed in the Netherlands is a combination of several techniques : dissolution, solvent extraction, ion exchange and electrolysis and in such a way and under such conditions, that no chemical wastes remain. The products can be obtained as salts or metals.

In the dissolution unit the solid waste is treated with 6M HCl at high temperature to dissolve all metals. The residue is filtered off. The solution is treated by MIBK to remove Fe^{3+} (if necessary after oxidation Fe^{2+} with air) ; backextraction gives $FeCl_3$ with high purity.

The raffinate is led through an anion exchange column. The metals Cu, Pb, Zn and Cd are fixed as chloride complexes, while Cr, Ni, Mn, Ca and Na past through. For the separation of Ni and Cr from this eluate several techniques are available, e.g. electrolysis ; afterwards Mn can be removed by precipitation.

The separation of the absorbed metals Cu, Pb, Zn and Cd takes place by elution with HCl solutions of decreasing strength. Recovery of HCl from Pb and Cu eluates takes place by distillation in the presence of sulphuric acid. Products are obtained as sulphates. HCl can be recycled within the process.

TNO - ion exchange process



sludges (Fe, Cr, Ni, Cu, Pb, Zn, Cd)
dissollution 6M HCl
HCl
concentrates (6M HCl)
filtration
inert residue
(Fe, Cr, Ni, Cu, Pb, Zn, Cd)
Fe - extraction
MIBK
back - extraction
FeCl3
(Cr, Ni, Cu, Pb, Zn, Cd)
H2SO4
0,5 M HCl
Cu
destillation
HCl
CuSO4
H2SO4
0,2 M HCl
Pb
destillation
HCl
PbSO4
anion exchange
H2SO4
0,005 M HCl
Zn
cation exchange
ZnSO4
H2SO4
H2O
Cd
cation exchange
CdSO4
(Cr, Ni)
H2SO4
destillation
HCl
(NiSO4, Cr2(SO4)3)
electrolysis
Cr
Ni

The Zn and Cd eluates can be treated by a cation exchanger in order to obtain sulphates.

If necessary electrolysis can be applied to obtain the materials in the metal form. The purity of the endproduct is very high : 99,9 %.

If necessary Co can also be recovered with this process.

An aspect of this process is, that liquid wastes can be put in directly without pretreatment (except the 6 M HCl conditions). Moreover a broad spectrum of wastes can be treated without leaving residues that have to be considered as hazardous.

C.A.11. COMPARISON OF THE PROCESSES : SOLVENT EXTRACTION AND SELECTIVE ION EXCHANGE

Revenues : Although the ion exchange process can recover more metals than the solvent extraction process, the revenues by treating a certain sludge is approximately the same. This is due to the fact that the revenues are determined by Cu, Ni, Zn and Cr and to a smaller extent by Fe, Pb and Cd. In both processes Cu, Ni and Zn are recovered. Generally the concentrations of Cd and Pb in sludges are relatively low. Based on the revenues the processes are practically equivalent.

Operating costs : Laboratory results allow only a rough estimation of these costs. From this estimation it can be gathered that the investment costs for the ion exchange process is about 60 to 70 % of the investment for the solvent extraction process at an average capacity of 15.000 tons/year (30 % dry matter). Concerning the running costs, the costs of chemicals for the solvent extraction process are highher (50 %) than those for ion exchange ; the energy costs of the ion exchange process, however, are unfavourable, if no use can be made of a waste energy source. As an example, the operating costs for the ion exchange process are roughly 400 F/ton sludge at a yearly capacity of 15.000 tons, exclusive the revenues of the products. The first evaluation of both processes shows roughly equal costs.

Separation spectrum : The ion exchange process shows a broader spectrum than the solvent extraction process. However, these extra separation possibilities have to be considered in the context of the composition of the wastes and the dumping problem as mentioned in the introduction.

Legislation : The composition of the solid residue is determined by the composition of the original waste and the process used. In general there will be a difference in the composition of the residues : the ion exchange process has a less contaminated one. This can be considered as an advantage, legislation with respect to dumping, being an important aspect.

ANNEX C - APPENDIX 2

COST PRICES OF EFFLUENT TREATMENT PROCESSES

(Refer to Annex B - Appendix 2)

....

CYANIDE OXIDATION - Cyanide oxidation costs are shown for continuous and batch treatment. Costing assumptions are :

A. For both continuous and batch treatment, the cyanide oxidation tank is sized as an above ground cylindrical tank with a retention time of 4 hours based on the process flow. Cyanide oxidation is normally done on a batch basis ; therefore, two identical tanks are employed.

B. Cyanide removal is accomplished by the addition of sodium hypochlorite. Sodium hydroxide is added to maintain the proper pH level. A 60 days supply of sodium hypochlorite is stored in an in-ground covered concrete tank, 0.305 meter (1 foot) thick. A 90 days supply of sodium hydroxide is also stored in an in-ground covered concrete tank, 0.305 meter (1 foot) thick.

C. Mixer power requirements for both continuous and batch treatment are based on 2 horsepower for every 3,000 gallons of tank volume. The mixer is assumed to be operational 25 per cent of the time that the treatment system is operating.

D. A continuous control system is costed for the continuous treatment alternative.

E. A complete manual control system is costed for the batch treatment alternative.

F. Manpower estimates for operation and maintenance reflect the varying schemes for continuous and batch operation.

For very small plating establishments, a completely manual treatment system may be used. This system consists of flat bottom, open top, standard resin fiberglass tanks that hold the daily flow. Chemicals are added manually at the end of each shift. For daily flow rates from1,893 to 37,850 liters per day, equipment costs range from $ 329 to $ 5,100.

CYANIDE OXIDATION - CONTINUOUS TREATMENT

Flow Rate (liters/hr)	3,785	5,678	7,570
Investment ($)	47,808	51,875	55,556
Annual costs :			
Capital costs	3,050	3,310	3,544
Depreciation	9,561	10,395	11,111
Operation and maintenance costs (excluding energy and power costs)	2,218	2,750	3,563
Energy and power costs	90	135	180
TOTAL ANNUAL COST ($)...............	14,920	16,570	18,098

CYANIDE OXIDATION - BATCH TREATMENT

Flow Rate (liters/Hr)	189	757	1,893
Investment ($)	10,325	13,258	17,069
Annual costs :			
Capital costs	659	846	1,089
Depreciation	2,065	2,652	3,414
Operation and maintenance costs (excluding energy and power costs)	464	1,854	4,636
Energy and power costs	5	18	45
TOTAL ANNUAL COST ($).........	3,192	5,370	9,184

CHROMIUM REDUCTION - Chromium reduction costs are presented for continuous treatment and for batch treatment. Costing assumptions are :

A. For both continuous and batch treatment, sulphuric acid is added for pH control. A 90 days supply is stored in the 25 per cent aqueous form in an above-ground, covered concrete tank, 0.305 meters (1 foot) thick.

B. For continuous chromium reduction, the single chromium reduction tank is sized as an above-ground cylindrical concrete tank with a 0.305 meter (1 foot) wall thickness, a 45 minute retention time, and an excess capacity factor of 1.2. Sulphur dioxide is added to convert the influent hexavalent chromium to the trivalent form.

C. A control system for continuous chromium reduction.

D. For batch chromium reduction, the dual chromium reduction tanks are sized as above-ground cylindrical concrete tanks, 0.305 meter (1 foot) thick, with a 4 hours retention time, and an excess capacity factor of 1.2. Sodium bisulphite is added to reduce the hexavalent chromium.

E. A completely manual system is provided for batch operation.

F. Manpower estimates for operation and maintenance reflect the varying schemes for continuous and batch operation.

G. A constant power requirement of 2 horsepower is assumed for chemical mixing.

For very small plating establishments, treatment may also be accomplished with a completely manual system. With this approach, flat bottom, open top, standard resin fiberglass tanks hold the daily flow and chemicals are added manually at the end of each shift. Equipment costs range from $ 329 to $ 5,100 for daily flow rates from 1,893 to 37,850 liters per day.

CHROMIUM REDUCTION - CONTINUOUS TREATMENT

Flow Rate (liters/Hr)	3,785	7,570	18,925
Investment ($)	20,416	21,538	24,003
Annual costs :			
Capital costs	1,303	1,374	1,531
Depreciation	4,083	4,308	4,801
Operation and maintenance costs (excluding energy and power costs)	1,086	1,375	2,089
Energy and power costs	256	256	256
TOTAL ANNUAL COSTS ($)............	6,728	7,313	8,677

CHROMIUM REDUCTION - BATCH TREATMENT

Flow Rate (liters/hr)	189	379	1,893
Investment ($)	8,493	9,535	14,405
Annual costs :			
Capital costs :	541	608	919
Depreciation	1,699	1,907	2,881
Operation and maintenance costs (excluding energy and power costs)	155	295	1,415
Energy and power costs	256	256	256
TOTAL ANNUAL COSTS ($)............	2,651	3,066	5,471

pH ADJUSTMENT - pH adjustment costs are presented. Costing assumptions are :

A. The pH adjustment tank is an in-ground concrete tank with a 45 minutes retention time. The tank has a length to width ratio of 5, a depth of 2.44 meters (8 feet), a thickness of 0.305 meter (1 foot), and an excess capacity factor of 1.2.
A mixer and tank excavation are included in the costs.

B. Lime is added to obtain the desired effluent pH. Mixer power is based on a representative installation with 1 turn over per minute.

Flow Rate (liters/Hr)	492	4,921	49,205
Investment ($)	1,452	4,921	18,855
Annual costs :			
Capital costs	93	314	1,203
Depreciation	290	984	3,771
Operation and maintenance costs (excluding energy and power costs)	286	1,036	3,758
Energy and power costs	8	79	1,503
TOTAL ANNUAL COST ($).................	677	2,413	10,315

CLARIFICATION - SETTLING TANK - Settling tank clarification costs are presented for continuous treatment and for batch treatment. Costing assumptions are :

A. For continuous clarification with an influent flow rate greater than or equal to 9,857 liters per hour (2,600 gallons/hour), costs include a concrete flocculator and its excavation, a concrete settling tank with skimmer and its excavation, and two centrifugal sludge pumps. For continuous clarification with influent flows less than 9,857 liters/hour (2,600 gallons/hour), costs include two above ground conical unlined carbon steel tanks and two centrifugal sludge pumps.

B. The flocculator size is based on a 45 minutes retention time, a length to width ratio of 5, a depth of 2.44 meters (8 feet), a thickness of 0.305 meters (1 foot), and an excess capacity factor of 1.2.
A mixer is included in the flocculator.

C. The settling tank is sized for a hydraulic loading of 1,356.7 liters/hour per square meter (33.3 gallongs/hour/sq.ft.), a 4 hours retention time, and an excess capacity factor of 1.2.

D. The two conical unlined carbon steel tanks are designed for a 4 hours retention time in each tank.

E. The sludge pumps are assumed operational one hour for each 12 hours of production and have 20 % excess pumping capacity. Costs include motors, starters, alternators, and necessary piping.

F. Lime and sodium sulphide are added for metal and solids removal. All power requirements are based on data from a major manufacturer.

G. For batch clarification, the dual centrifugal sludge pumps and the chemical demands are identical to continuous clarification. However, the flocculator and settling tank are replaced with dual above ground cylindrical carbon steel tanks.

H. Each tank is sized by an 8 hours retention time and an excess capacity factor of 1.2. Each tank has a mixer that operates 1 hour for each 8 hours that the tank is being used.

I. Manpower estimates for operation and maintenance reflect the varying schemes for continuous and batch treatment.

CLARIFICATION - CONTINUOUS TREATMENT SETTLING TANK

Flow Rate (liters/Hr)	37,850	75,700	157,708
Investment ($)	71,363	91,575	130,102
Annual costs :			
Capital costs	4,552	5,842	8,301
Depreciation	14,273	18,315	26,020
Operation and maintenance costs (excluding energy and power costs)	2,506	2,565	3,851
Energy and power costs	36	72	150
TOTAL ANNUAL COST ($)....................	21,367	26,794	38,322

CLARIFICATION - BATCH TREATMENT SETTLING TANK

Flow Rate (liters/hr)	1,893	3,785	18,925
Investment ($)	25,551	28,529	38,032
Annual costs :			
Capital costs	1,630	1,820	2,427
Depreciation	5,110	5,706	7,606
Operation and maintenance costs (excluding energy and power costs)	2,334	2,341	2,394
Energy and power costs	41	81	811
TOTAL ANNUAL COST ($)...................	9,155	9,948	13,238

DIATOMACEOUS EARTH FILTRATION - Diatomaceous earth filtration costs are presented. Costing assumptions are :

A. Unit cost is based on one filter station comprised of one filter, one mix tank, two pumps, and associated valving. The unit is shut down one hour each day of operation for cleaning and filter precoating.

B. Diatomaceous earth addition rates, power requirements, and manpower requirements are based on manufacturer's data.

Flow Rate (liters/Hr)	189	4,731	47,313
Investment ($)	8,823	27,707	62,819
Annual costs :			
Capital costs	563	1,768	4,008
Depreciation	1,765	5,541	12,564
Operation and maintenance costs (excluding energy and power costs)	3,936	6,046	29,872
Energy and power costs	22	302	1,970
TOTAL ANNUAL COST ($).................	6,286	13,657	48,414

SYSTEM COST ESTIMATES (END OF PIPE TREATMENT)

Sludge drying beds are used for sludge dewatering. The dewatered sludge is removed by a contractor and deposited in a secure landfill. A sludge bed loading of 0.318 liter par hour per square meter (0.0078 gallon per hour per square foot) with a bed excavated to a depth of 1.2 meters (4 feet) and an excess capacity factor of 1.5 are used to calculate the required dying bed area. This unit is not sized for any influent flow rate less than 189 liters per day (50 gallons per day) as the bed area becomes too small to warrant construction. Separated water is recycled to the clarifier inlet. Since this volume flow is so low, it is ignored when calculating the clarification costs.

Table presents costs for the end-of-pipe treatment system for various treatment system influent flow rates for a plant with no electroless plating operations. A plant with electroless plating operations would require a separate clarifier for the segregated chelated waste stream. The basic cost elements used in preparing this table are the same as those presented for the individual technologies : investment, annual capital cost, annual depreciation, annual operation and maintenance cost (less energy and power cost), energy and power cost, and total annual cost. These elements were discussed in detail earlier in this section. Investment and annual operation and maintenance cost (less energy and power cost) are divided into waste water treatment and sludge handling categories. Table presents end-of-pipe treatment system costs where the separate clarifier is required for the segregated chelated waste stream.

For the cost computation, a "least cost" treatment system selection is performed. This procedure calculates the costs for a batch treatment system, a continuous treatment system, and haulaway of the complete waste water flow over a 10 year comparison period and selects the cheapest system. A typical "least cost" treatment system is indicated on tables for the conditions outlined below.

The various investment costs assume that the treatment system must be specially constructed and include all subsidiary costs discussed under the Cost Breakdown Factors segment of this section. Operation and maintenance costs assume continuous operation, 24 hours a day, 5 days per week, for 52 weeks per year. The typical waste loads and treatment system influent flow rates were based on the results of detailed waste and production analyses of the plants surveyed. Chromium and cyanide bearing wastes are each approximately 10 % of the total plant waste water discharge. When chelated wastes are present, they may amount to approximately 10 % of the raw waste loading. The remainder of the waste water flow appears as the common acid -alkaline stream. The total waste water flow rates presented on tables are identical. However, chelated wastes have different parameter concentrations than the other waste streams. Therefore, a mass balance does not exist between tables and the costs in these two tables are not directly comparable.

END-OF-PIPE TREATMENT WITHOUT CHELATED WASTES

Total Flow Rate (liters/Hr)	7,885	23,655	236,562
Least Cost System	batch	batch	continuous
Investment Costs :			
Waste water Treatment ($)	96,142	145,166	431,143
Sludge Handling	0	0	17,361
Total Investment ($)	96,142	145,166	448,504
Annual costs :			
Capital costs	6,134	9,261	28,614
Depreciation	19,228	29,033	89,701
Operation and maintenance costs (excluding energy & power costs)			
Waste water treatment	7,555	19,731	33,267
Sludge Handling	0	0	4,172
Total O and M	7,555	19,731	37,439
Energy and power costs	627	1,341	1,057
TOTAL ANNUAL COSTS ($)..................	33,545	59,367	156,810

END-OF-PIPE TREATMENT WITH CHELATED WASTES

Total Flow Rate (liters/Hr)	7,885	23,655	236,563
Least Cost System	batch	batch	continuous
Investment Costs :			
Waste water Treatment ($)	129,269	183,313	516,802
Sludge Handling	0	0	17,284
Total Investment ($)	129,269	183,313	534,086
Annual costs :			
Capital costs	8,247	11,695	34,074
Depreciation	25,854	36,663	106,817
Operation and maintenance costs (excluding energy and power costs)			
Waste water treatment	9,904	22,122	36,041
Sludge Handling	0	0	4,197
Total O and M	9,904	22,122	40,238
Energy and Power costs	611	1,291	1,057
TOTAL ANNUAL COSTS ($)..................	44,615	71,770	182,186

The actual costs of installing and operating an end-of-pipe treatment system at a particular plant may be substantially below the tabulated values.

Reductions in investment and operating costs are possible in several areas. Design and installation costs may be reduced by using plant engineering and maintenance personnel instead of contracting the work. Equipment costs may be reduced by using or modifying existing equipment instead of purchasing all new equipment. Application of an excess capacity factor, which increases the size of most equipment to compensate for shutdowns, may be unnecessary. Excavation and foundations costs could be reduced if an existing concrete pad or floor can be utilized. Equipment size requirements may be reduced by the ease of treatment (for example, shorter retention time) of particular waste streams. Substantial reductions in both investment and operating cost could be realized if a plant reduced its water use rate by various in-plant techniques. Then, to estimate its costs from the tables, the plant would use the projected flow rate rather than the current flow rate. If a plant has lower raw waste concentrations than those indicated in Section V, investment and, in particular, operating costs will be lower. The tabulated costs are based on around-the-clock operation 260 days per year. Thus, if a plant operates one or two shifts per day or has an annual shutdown period operation, costs would be significantly lower. In some parts of the country, operating costs would be lower because of wage rates lower than the values used in the computations. Reductions in labour cost by using operating and maintenance personnel on a shared (part time) basis may also be practical.

The results of the cost program executions are estimated to be nominally accurate to ± 12 %. Comparison by an independent contractor of the cost program output to actual plant data for comparable waste water treatment equipment indicates that this range of accurcy is being obtained.